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THE UNIVERSITY OF ALBERTA

PROGRAMMED TEMPERATURE TIME NORMALIZATION GAS CHROMATOGRAPHY

by

© Ervin A. Prommer

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

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OF MASTER OF SCIENCE

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EDMONTON, ALBERTA

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FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled PROGRAMMED TEMPERATURE TIME NORMALIZATION GAS CHROMATOGRAPHY submitted by E.A. Prommer in partial fulfilment of the requirements for the degree of Master of Science.

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Supervisor

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July 16, 1973

Date.....

ABSTRACT

Optimum resolution was determined for a series of straight chain hydrocarbons under time normalization. The variable parameters were programmed temperature rate, isothermal temperature, normalized net retention time, helium flow rate, and column length. The percent liquid phase in each column was such that the total amount of liquid phase remained constant for each column in a series of varying column lengths. The results showed that if one worked with an amount of liquid phase normally packed into a one meter column using 25 percent liquid phase packing, the resolution varied by less than one unit when the column length varied from approximately 1.5 to 5.0 meters for the separation of a given pair of straight chain hydrocarbons, for a given helium flow rate and for a given programmed temperature rate. For column lengths less than approximately 1.5 meters, the resolution decreased sharply with decreasing column length. The optimum programmed temperature rate was dependent on the compounds being examined e.g. as the straight chain hydrocarbon number increased the optimum programmed temperature rate decreased. For all the normalized net retention times, column lengths and hydrocarbon numbers, the resolution increased with helium flow rate.

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PRINCIPAL SYMBOLS

d_f	Liquid film thickness
D_g	Diffusion coefficient of solute in gas phase
D_l	Diffusion coefficient of solute in liquid phase
H	HETP
j	Compressibility correction factor
k	Capacity ratio
L	Column length
M_1	Molecular weight of eluent gas
M_2	Molecular weight of diffusing solute
P_i	Inlet column pressure
P_o	Outlet column pressure
q	Configuration constant
S	Surface area of solid support
T	Temperature
T_{c1}	Critical temperature of eluent gas
T_{c2}	Critical temperature of diffusing solute
t_R	Retention time
u	Average gas velocity
u_o	Gas velocity at column outlet
V_{c1}	Critical volume of eluent gas
V_{c2}	Critical volume of diffusing solute
w	Baseline peak width
α	Relative net retention time
γ	Tortuosity factor or obstruction factor
ρ_s	Density of stationary phase
%	Percent liquid phase on the solid support

PART I

INTRODUCTION

In time normalization the parameters of the gas chromatographic system are such that the last component of the separated sample comes out of the column with a fixed net retention time as one or more parameters are changed. This gas chromatographic technique has received relatively little attention in the field of gas-liquid chromatography. The first experimental work using time normalization was done by Karger and Cooke (1), who showed that for maximum resolution under normalized time conditions an optimum column length exists for both packed and capillary columns. The column used was a 1/8 in., o.d., copper tubing packed with 30/60 mesh Chromosorb PH coated with 3 percent Dow 710 silicone oil. The sample injected was 0.2 μl of 1 percent (1 to 1) dodecane and tetradecane in n-hexane.

The optimum length for maximum resolution for normalized retention times of 1200 ± 60 seconds and 2860 ± 90 seconds for tetradecane was 30 feet and 55 feet. The optimum length for maximum resolution under isothermal conditions of 130°C was 80 feet.

In the same experiment a capillary column was prepared by evaporation of a 10 percent solution of silicone

oil. When both capillary and packed columns were normalized to a retention time of 1200 seconds the optimum length for maximum resolution were 150 feet and 30 feet.

In another publication (2) by the same authors the particle size and average carrier gas velocity were also optimized under normalized time conditions. The effect of mesh size on resolution was examined under constant inlet pressure and constant average carrier gas velocity under time normalization. Five columns of Chromosorb P with mesh sizes 45/60, 60/80, 80/100, 100/120, and 120/140 each coated with 4 percent Dow 710 silicone oil were prepared. When a solute such as 2-methylnaphthalene with a low relative retention dependence on temperature or a solute such as n-octane with a high relative retention dependence on temperature was injected it was found that large particles (45/60 mesh) were best for low inlet pressures (low flow rates) and small particles (120/140 mesh) were best for high inlet pressures (high flow rates).

In a study where average velocity was kept constant they used a column of constant length and 4 percent Dow 710 silicone oil. When solutes such as the methylnaphthalenes were injected under isothermal and normalized time conditions, resolution increased with decreasing particle size until 80/100 mesh. With further decrease in particle size the resolution remained constant.

When solutes such as the iso-octanes with a high relative retention dependence on temperature were injected under constant average velocity and normalized time conditions resolution was about the same for large (45/60 mesh) and for small (120/140 mesh) particles.

For normalized times of 134 and 186 seconds, the resolution for mesh sizes 45/60 and 120/140 were almost equivalent, while for the normalized time of 94 seconds the resolution for mesh size 45/60 was 9 percent higher than for mesh size 120/140. The authors concluded that under constant average velocity and normalized time conditions "a better resolution is possible without loss in retention time by operation above the velocity for H_{min} with a simultaneous reduction in temperature" (2).

Grushka, Yepes-Baraya and Cooke (3) showed the effect of temperature, carrier gas velocity and amount of stationary phase on resolution under normalized time conditions. Packed columns used were 2m x 1/8 in., o.d., copper tubing, packed with 3 to 30 percent w/w Apiezon L on 80/100 mesh AWDMCS Chromosorb W. Capillary columns were made from a 316 stainless steel 0.01 in., i.d., 150 feet in length and coated with 17 percent w/w Apiezon L in toluene. When experimental runs with this length of column were completed, the column was cut in such a way as to yield a 50 foot and a 100 foot column.

Sample mixtures used for the packed columns were: a) 1 cc of 3-methylnonane and 1 cc of 5-methylnonane diluted to 25 cc with acetone; b) 1 cc of sec-butylbenzene and 1 cc of tert-butylbenzene diluted to 25 cc with benzene. Mixtures used for the capillary columns were 3-methylnonane and decane and a mixture of 1-methylnaphthalene and 2-methylnaphthalene. 1 μl amounts of these solutions were injected.

Increasing percent liquid phase at constant temperature and velocity for the 3-methylnonane/decane mixture on 50 ft capillary columns showed that an optimum range of liquid film thickness d_f exists in which the resolution is maximized ($d_f \cong 0.4\mu$). Increasing percent liquid phase on packed columns at constant velocity and temperature showed that the increase in resolution with percent liquid phase was not as great as for the capillary columns. The resolution of the methylnonanes was approximately the same on all their columns while the resolution of the butylbenzenes showed a small maximum.

Under time normalization for the decane/3-methylnonane mixture on capillary columns at constant velocity and retention time of 211.3 seconds the results showed that the resolution decreased with increasing percent liquid phase and temperature in spite of an initial decrease in H (minimum at $d_f \cong 0.4\mu$) for decane. For packed

columns under time normalization for the 3- and 5-methylnonanes the results showed that the resolution also decreased with increasing percent liquid phase. They concluded that resolution is best for the lower loaded column operated at a lower temperature.

Under time normalization where velocity instead of temperature is changed for both capillary and packed columns the results showed that an optimum range exists in the amount of stationary phase and in the velocities of the gas phase. For capillary columns the optimum film thickness was approximately 0.35μ with the carrier velocity about 47 cm/sec. For packed columns maximum resolution occurred at about 5 percent loading at about 7.9 cm/sec. Their theoretical equation indicated a maximum resolution at a liquid film thickness of 0.3μ and a carrier velocity of about 46.5 cm/sec for the capillary column and a maximum resolution a 3.5 percent liquid loading and carrier velocity at about 6 cm/sec for the packed column. In all the cases above the optimum liquid phase loadings and velocities were simultaneously at the optimum.

Grushka, Yepes-Baraya and Cooke (3) derived an equation from $R = 1/4(L/H_2)^{1/2}(\alpha-1/\alpha)(k_2/k_2+1)$ in which they substituted a simplified van Deemter equation for $H_2 = 2\gamma D_g/u + qd_f^2k_2u/D_1(k_2+1)^2$ where L = column length,

α = relative net retention time, k_2 = capacity ratio for the second peak, γ = a correction factor to allow for the sinusoidal paths traversed by the carrier gas in the column (also known as the tortuosity factor or obstruction factor and having a value of 0.5 - 0.7), D_g = the diffusion coefficient of the solute in the gas phase, u = the carrier gas average velocity, q = a geometric factor known as a configuration constant the value of which depends upon the shape of the liquid phase pool (assuming a uniform film thickness, q has a value of 2/3), d_f = the film thickness, and D_l = the diffusion coefficient of the solute in the liquid phase.

The assumptions made were: a) the eddy diffusion term and the resistance to mass transfer i.e. the radial (gas resistance) diffusion term are vanishingly small; b) the capacity ratio is proportional to the percent liquid phase, i.e. $k_2 = a(\%)$; and c) the film thickness d_f is given by $d_f = \%/S\rho_s$ where % = the percent of liquid phase on the packing, S = the surface area per gram of the support, and ρ_s = the density of the stationary phase.

Substituting the simplified van Deemter equation for H_2 into the equation for R and then substituting the equation for $u = ju_o = L(1+k_2)/t_{R2}$ (where t_{R2} = the normalized retention time for the second peak, u = the average gas velocity, u_o = the gas velocity at the column outlet

and J = the compressibility correction factor) one then obtains

$$R = \frac{1/4\sqrt{L}\,(k_2/k_2+1)(\alpha-1/\alpha)}{\sqrt{\frac{2\gamma D_g t_{R2}}{L(k_2+1)} + \frac{2k_2L(\%)^2}{3D_1t_{R2}(k_2+1)(S\rho_s)^2}}}$$

which reduces to

$$R = \frac{1/4\sqrt{L}\,k_2(\alpha-1/\alpha)}{\sqrt{\frac{2\gamma D_g t_{R2}(k_2+1)}{L} + \frac{2k_2L(k_2+1)(\%)^2}{3D_1t_{R2}(S\rho_s)^2}}}$$

Using $k_2 = a(\%)$, R becomes

$$R = \frac{1/4\sqrt{L}\,(a\%)(\alpha-1/\alpha)}{\sqrt{\frac{2\gamma D_g t_{R2}(a\%+1)}{L} + \frac{2La(\%)^3(a\%+1)}{3D_1t_{R2}(S\rho_s)^2}}}$$

which is the equation derived by Grushka, Yepes-Baraya and Cooke (3) and was used to describe experimental results for packed columns under normalized time conditions.

The columns used in previous experimental work were either of constant length (2,3) or where various column lengths were used (1) the amount of liquid phase inside the column increased with column length. In my work attention was focused on a series of columns of varying

lengths, each column containing the same amount of liquid phase. Time normalization was applied to the determination of maximum resolution when column length, helium flow rate, isothermal temperature, and programmed temperature rates were varied for a sample containing a series of straight chain hydrocarbons.

PART II

EXPERIMENTAL AND EQUIPMENT USED

1 EXPERIMENTAL

The liquid phase selected was UCW98. The solid support was unsilanized Chromosorb WAW 60/80 mesh. The column was 1/8 in., o.d., Anaconda soft copper tubing.

A 5%, 8.3%, 25%, and 50% liquid loading on solid support was prepared by dissolving 0.60g, 1.00g, 2.96g, and 6.02g UCW98 in diethyl ether and added to 12.07g (50.29 ml), 12.03g (50.14 ml), 11.85g (49.37 ml), and 12.05g (50.21 ml) of Chromosorb WAW 60/80 mesh. Four columns of lengths 5.0m, 3.0m, 1.0m, and 0.5m were cleaned with acetone, allowed to dry and were filled with the 5.0%, 8.3%, 25.0%, and 50.0% packing using the gravity method. In this method the dry coated support is slowly poured through a funnel into the vertical tubing while gently tapping or vibrating the column (4). The columns were then bent into 8 inch diameter coils. The 5.0m column was made from two 2.5m lengths and were connected by 1/8 inch Swagelok unions. Quartz wool was used to plug the ends of the copper tubing. Each column then contained 0.144g of liquid phase, calculated as (vol. of column / vol. of packing prepared) x wt of liquid phase used to prepare the packing. An equivalent set of four columns was prepared and used as reference columns. Before use each

column was conditioned at 200°C for 10 hours during which a helium flow was maintained. After conditioning, approximately 40 µl of a GLC Column Conditioner (Silyl·8, Pierce Chemical Co., P.O. Box 117, Rockford, Illinois) was injected into each column at 200°C. The treatment was repeated once after a 5 minute interval.

A 10 µl Hamilton syringe was used to inject a sample size of 0.2 µl n-nonane, n-decane, n-hendecane, and n-dodecane with relative peak areas 1.0, 1.57, 2.56, and 4.59. The same sample size with the four components mentioned above was used throughout the experiment. The gas chromatographic peaks were digitized using a digital integrator with printer. The digitized peaks were then analyzed by an IBM 360/67 computer which then calculated HETP and resolution using a Fortran program which appears at the end of this report.

Helium flow rates were measured with a soap bubble flow meter at 25°C and were corrected for water vapor pressure in the flow meter by the formula $V_c = V_o(P_a - P_w)/P_a$ where V_c = corrected flow rate at outlet column pressure, V_o = flow rate measured with soap bubble flow meter at outlet column pressure, P_a = atmospheric pressure, and P_w = the vapor pressure of water at 25°C. All retention times were measured with outlet column at atmospheric pressure and were not corrected with the compressibility factor j.

Time normalization coupled with a wide variation of programmed temperature rates and a wide variation of net retention times necessitates a wide variation of initial temperatures for the column. However with the temperature programmer used in this study, initial temperatures were restricted to those above room temperature. The large size of the oven used restricted the heating rate to less than 14 deg/min. These restrictive conditions resulted in some graphs which appear to be incomplete.

2 EQUIPMENT USED

The gas chromatographic system was constructed from separate units of equipment. A schematic diagram of the system is given in Figure 1.

A. Brooks flow controllers.

B. Injection block - one in which the helium passed close to the septum.

C. A.P.I. two mode controller - A.P.I Instruments Co. It controlled the temperature of the injection block at 200°C.

D. Programmer - Varian Aerograph Linear Temperature Programmer Model 330.

E. Column of 1/8 in., o.d., copper tubing of varying lengths packed with UCW98 liquid phase (Hewlett-Packard) on Chromosorb WAW 60/80 mesh (Hewlett-Packard, Avondale Division).

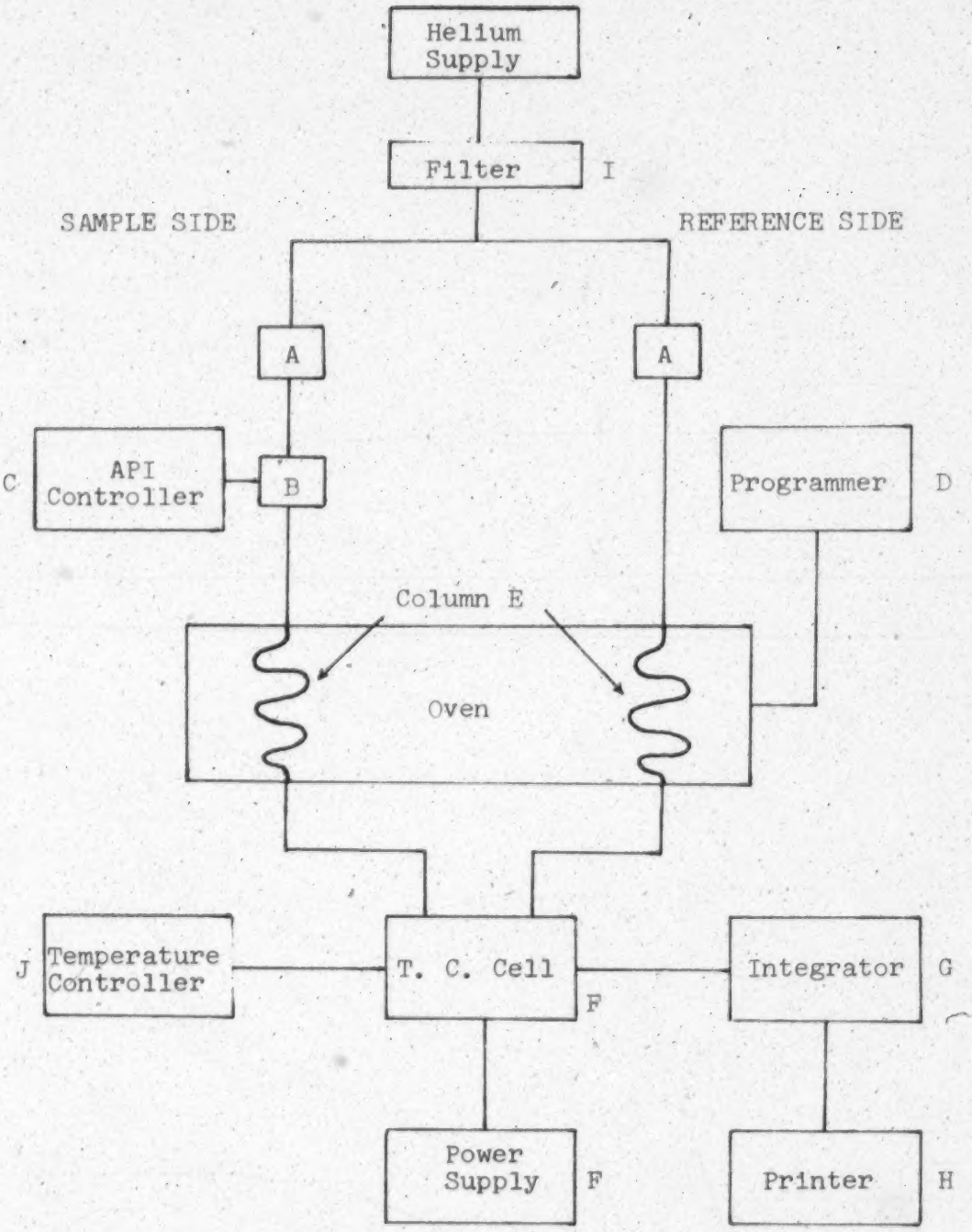

Fig. 1 The gas chromatographic system

F. Gow-Mac power supply, Model 40-05-C, and Gow-Mac thermal conductivity cell, Model 9285-D, Gow-Mac Instrument Co., Madison, New Jersey. The detector current was 180 ma.

G. Aerograph digital integrator - Model 471-42 - manufactured by Infotronics Corp., Houston, Texas.

H. Victor digit-matic printer - Victor Comptometer Corp., Chicago, Illinois.

I. Filter - Trap number 236 - Guild Corporation, Bethel Park, Pa., U.S.A.

J. Temperature Controller - RFL Model 70-115/208/230V - R.F.L. Industries, Inc., Boonton, New Jersey, U.S.A.

PART III

RESULTS AND DISCUSSION

1 HETP vs Helium Flow Rate

Fig. 2 shows the effect of isothermal temperature, column length, straight chain hydrocarbon number, and helium flow rate on HETP. The three isothermal temperatures selected were 95°C, 110°C and 125°C. In all the cases shown the HETP decreased with isothermal temperature from 125°C to 95°C. For a given isothermal temperature increase, the percent increase in HETP increased as the column length increased and as the straight chain hydrocarbon number decreased e.g. for a change of 15°C in the isothermal temperature, the change in HETP for n-nonane was dramatic while for n-dodecane the change in HETP was insignificant. This can be explained as follows. HETP, column length, resolution, the relative volatility α, and the capacity factor k are related by the equation (1) $HETP = (L/16R^2)(\alpha-1/\alpha)^2(k/k+1)^2$. The ratios $\alpha-1/\alpha$ and $k/k+1$ change most when α is close to 1 and when k is small i.e. when the column temperature is near the boiling point of a sample component. In this experiment the column temperature was nearest the boiling point of n-nonane and farthest from the boiling point of n-dodecane. For a given column length e.g. 5.0m and e.g. isothermal temperature at 125°C and helium flow rate 21 ml/min,

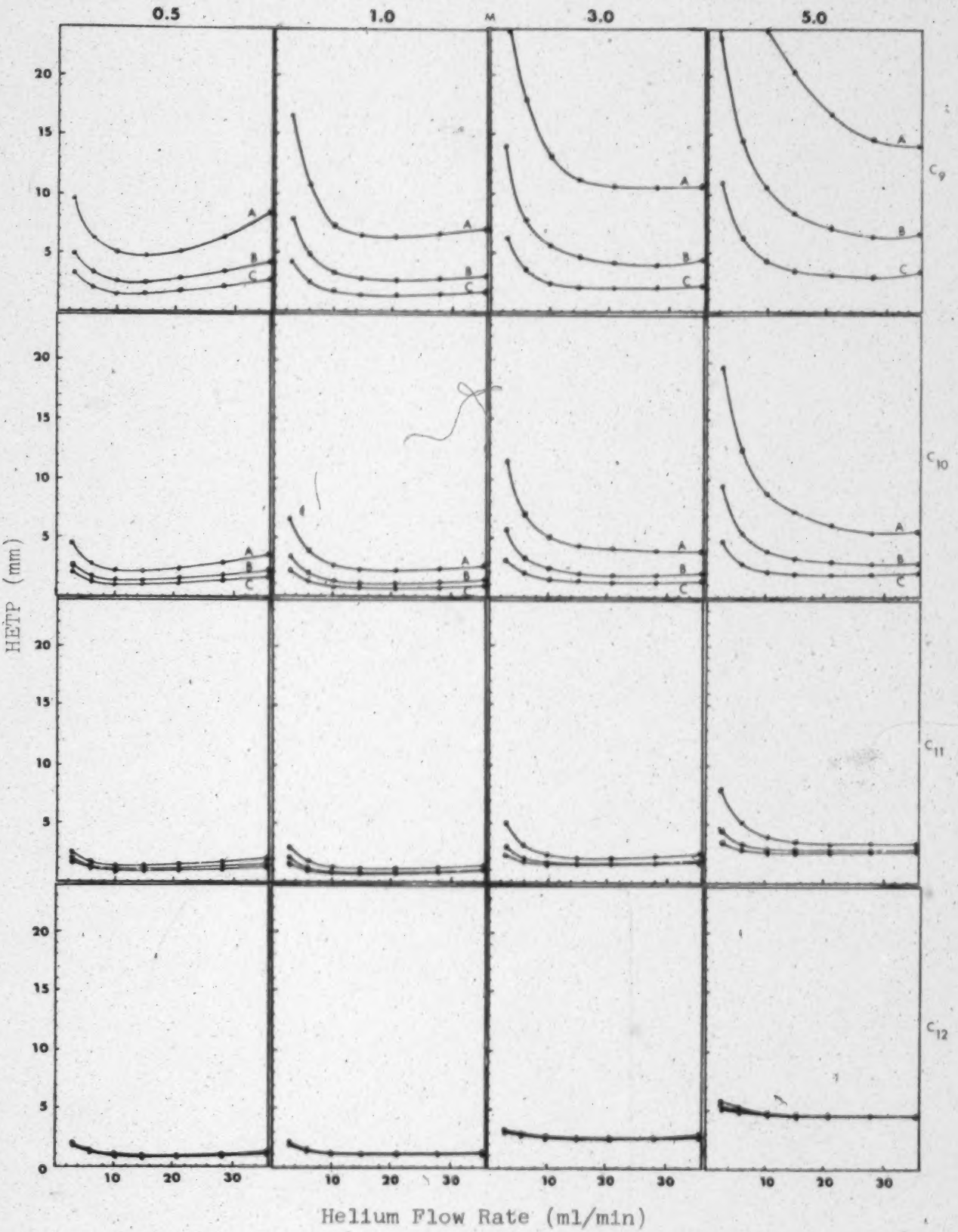

Fig. 2 HETP vs Helium flow rate. Columns from left

to right are for column lengths of 0.5, 1.0, 3.0, and 5.0 meters. Rows from top to bottom are for n-nonane, n-decane, n-hendecane, and n-dodecane. A, B and C are isothermal temperatures of 125°C, 110°C and 95°C.

the HETP decreased as the hydrocarbon number increased. The resolutions at 125°C for C_9-C_{10}, C_{10}-C_{11} and C_{11}-C_{12} were 3.26, 4.86 and 5.02. The capacity ratios at 125°C for C_9, C_{10}, C_{11}, and C_{12} were 0.7, 1.28, 2.32, and 4.23. The ratios k/k+1 at the same temperature for the same series were 0.411, 0.561, 0.698, and 0.808. The changes $\Delta(k/k+1)$ for C_9-C_{10}, C_{10}-C_{11} and C_{11}-C_{12} were 0.150, 0.137 and 0.110. The change in resolution ΔR between C_9-C_{10} and C_{10}-C_{11} was 1.60 and between C_{10}-C_{11} and C_{11}-C_{12} was 0.16. The value of α for all the hydrocarbons was approximately 1.8 since temperature was constant and the change $\Delta\alpha$ from one hydrocarbon to the next will be considered negligible. Therefore the change in HETP will increase as the hydrocarbon number decreases i.e. the HETP changes most for n-nonane and least for n-dodecane. This was experimentally observed in Figure 2.

With a few exceptions the absolute value of HETP increased as the column length increased from 0.5 meters to 5.0 meters. For the exceptions, which were 95°C for n-nonane, 95°C and 110°C for n-decane and 95°C, 110°C and 125°C for n-hendecane, the HETP decreased slightly (less than 0.3mm) when the column length increased from 0.5 meters to 1.0 meter and then the HETP increased signi-

ficantly when the column length increased further from 1.0 meter to 5.0 meters.

The optimum helium flow rate increased with column length and was independent of the straight chain hydrocarbon number. For example the optimum helium flow rate for the 0.5 meter column for n-nonane, n-decane, n-hendecane, and n-dodecane was approximately 13 ml/min and for the 5.0 meter column for the same straight chain hydrocarbons the optimum helium flow rate was approximately 30 ml/min. As the straight chain hydrocarbon number increased the optimum flow rate became less definable. The HETP plot for n-dodecane for example was almost independent of helium flow rate.

From the van Deemter plots in Fig. 2 one can deduce that the optimum parameters are a column length of approximately 1 meter, an isothermal temperature of 95°C and a helium flow rate of approximately 20 ml/min.

2 Resolution vs Helium Flow Rate

Fig. 3 shows the effect of helium flow rate, column length and isothermal temperature on the separation of n-nonane, n-decane, n-hendecane, and n-dodecane. In all the cases shown the resolution increased as the temperature decreased from 125°C to 95°C at 15°C intervals. For a given decrease in the isothermal temperature, the

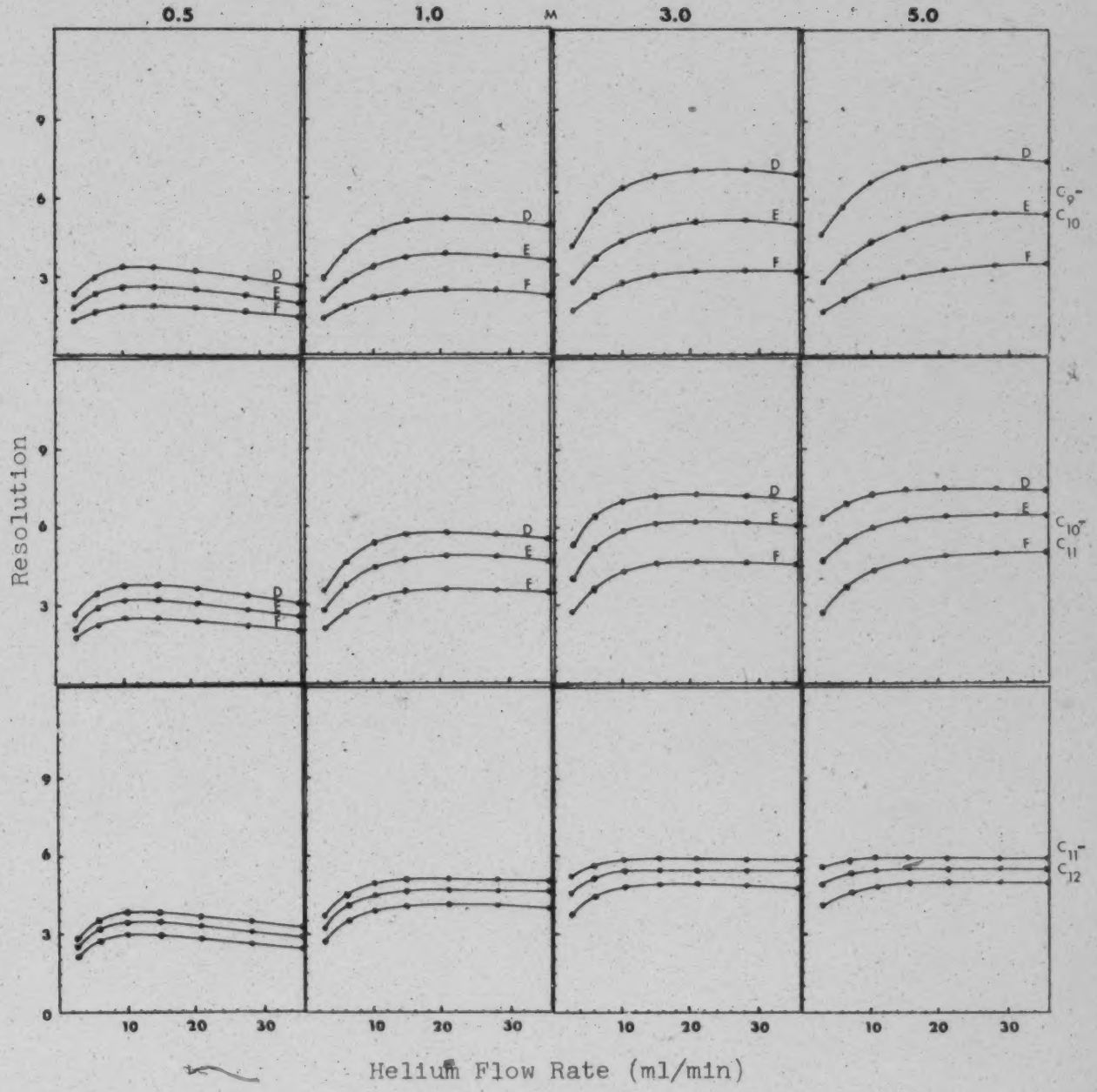

Fig. 3 Resolution vs helium flow rate. Columns from left to right are for column lengths of 0.5, 1.0, 3.0, and 5.0 meters. Rows from top to bottom are for n-nonane-decane, n-decane-hendecane and n-hendecane-dodecane. D, E and F are for isothermal temperatures of 95°C, 110°C and 125°C.

percent increase in the resolution increased as the column length increased and as the straight chain hydrocarbon number decreased e.g. for a change of 15°C in the isothermal temperature, the change in resolution for n-nonane-decane for a given column length was greater than the change in resolution for n-hendecane-dodecane at the same column length. For all three isothermal temperatures and all the straight chain hydrocarbons the absolute value of the resolution increased with column length from 0.5 meters to 5.0 meters although there was no significant increase when column length increased from 3.0 meters to 5.0 meters where it appears to have reached a limiting or optimum value.

The optimum helium flow rate increased with column length and was independent of the straight chain hydrocarbon number. For example the optimum helium flow rate for the 0.5 meter column for the separation of n-nonane-decane, n-decane-hendecane and n-hendecane-dodecane was approximately 13 ml/min and for the 5.0 meter column for the same straight chain hydrocarbons the optimum helium flow rate was approximately 30 ml/min.

For the separation of a given straight chain hydrocarbon, for a given column length and for a given isothermal temperature the resolution changed by less than one unit when the helium flow rate varied from approximately 10 ml/min to 36 ml/min.

From the plots in Fig. 3 the optimum parameters are a column length of about 4 meters, an isothermal temperature of 95°C and a helium flow rate of approximately 20 ml/min. The optimum temperature and optimum helium flow rate are in agreement with the van Deemter plots in Fig. 2. However the resolution vs helium flow rate plots in Fig. 3 indicate an optimum column length of 4 meters while the van Deemter plots in Fig. 2 indicate an optimum column length of 1 meter. Here we have a case where HETP and resolution both increase with column length.

3 Time Normalization With Net Retention Time For N-Dodecane Fixed at 300 ± 5 Seconds

Figs. 4, 5 and 6 show the effect of helium flow rate, column length, isothermal temperature, and programmed temperature rate on the resolution of n-nonane, n-decane, n-hendecane, and n-dodecane when the net retention time for n-dodecane was fixed at 300 ± 5 seconds.

The three helium flow rates used were 6.8, 13.5 and 20.3 ml/min. In all the cases shown the resolution increased as the helium flow rate increased from 6.8 ml/min to 20.3 ml/min at spaced ml/min intervals. With an increase of helium flow rate from 6.8 ml/min to 13.5 ml/min the increase in resolution was dependent on column length but not on the hydrocarbon number. For column lengths 1.0 meter to 5.0 meters the increase in resolution for n-nonane-decane, n-decane-hendecane and n-hendecane-dodecane was approximately 1.5 units. For column length 0.5 meters the increase in resolution for the same series of compounds was approximately 1.0 unit.

For an increase of helium flow rate from 13.5 ml/min to 20.3 ml/min the increase in resolution was dependent on column length and on the hydrocarbon number. For column lengths 1.0 meter to 5.0 meters the increase in resolution for n-nonane-decane, n-decane-hendecane was approximately 0.75 units. The increase in resolution

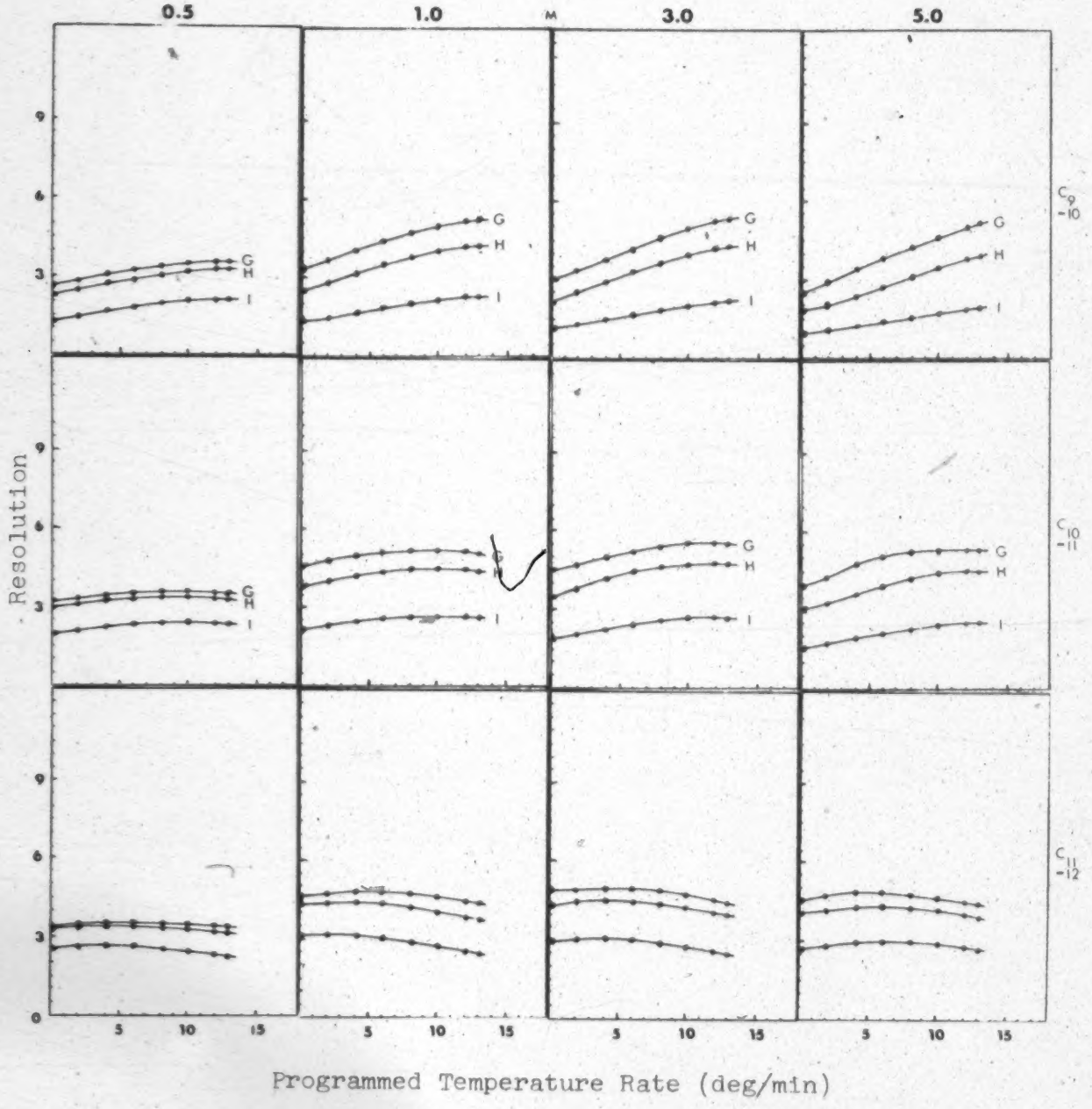

Fig. 4 Resolution vs programmed temperature rate when normalized net retention time for n-dodecane was fixed at 300 ± 5 seconds. Columns from left to right are for column lengths of 0.5, 1.0, 3.0, and 5.0 meters. Rows from top to bottom are for n-nonane-decane, n-decane-hendecane and n-hendecane-dodecane. G, H and I are for helium flow rates of 20.3, 13.5 and 6.8 ml/min.

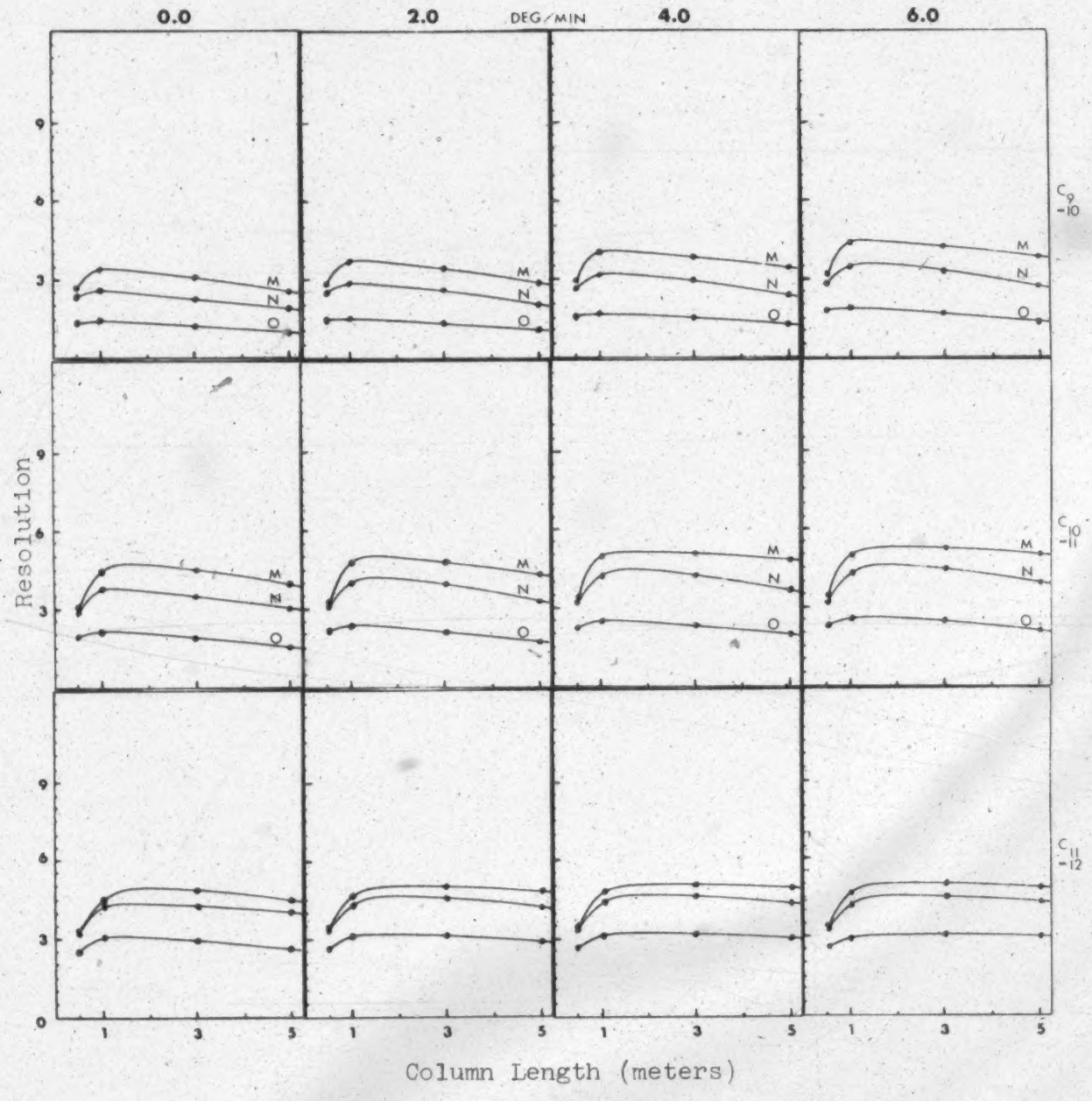

Fig. 5 Resolution vs column length when normalized net retention time for n-dodecane was fixed at 300 ± 5 sec. Columns from left to right are for programmed temperature rates of 0.0 (isothermal), 2.0, 4.0, and 6.0 deg/min. Rows from top to bottom are for n-nonane-decane, n-decane-hendecane and n-hendecane-dodecane. M, N and O are for helium flow rates of 20.3, 13.5 and 6.8 ml/min.

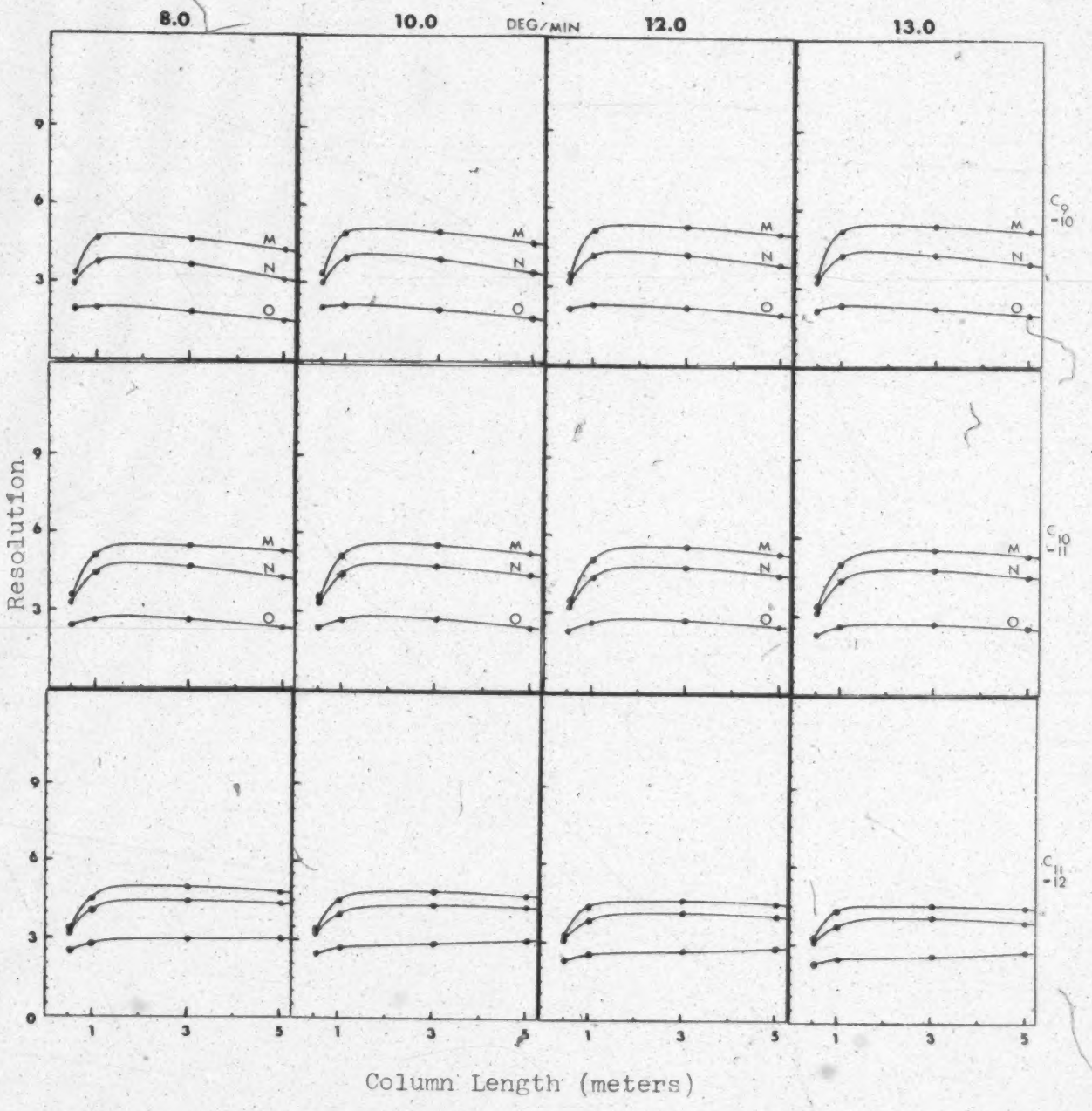

Fig. 6 Same as Fig. 5 except columns from left to right are for programmed temperature rates of 8.0, 10.0, 12.0, and 13.0 deg/min.

for n-hendecane-dodecane was approximately 0.5 units. For column length 0.5 meters the increases in resolution for n-nonane-decane, n-decane-hendecane and n-hendecane-dodecane were approximately 0.4, 0.25 and 0.15 units. For a given pair of straight chain hydrocarbons and for a given increase in helium flow rate in the 6.8 ml/min to 20.3 ml/min range, the increase in resolution was independent of column length within the 1.0 to 5.0 meter range.

For the separation of a given pair of straight chain hydrocarbons, for a given helium flow rate (6.8 - 20.3 ml/min) and for a given programmed temperature rate (0.0 - 13.0 deg/min) the resolution varied by less than one unit when the column length varied from approximately 1.5 meters to 5.0 meters. The resolution dropped sharply by several units when the column length decreased from approximately 1.5 meters to 0.5 meters i.e. when the percent liquid phase increased from approximately 19 to 50 percent.

The optimum programmed temperature rate was dependent on which pair of straight chain hydrocarbons was being separated. As the straight chain hydrocarbon number increased the optimum programmed temperature rate decreased. For the separation of n-nonane-decane the resolution for all three helium flow rates increased gradually as the programmed temperature rate increased from 0.0 deg/min (isothermal) to 13.0 deg/min. By extrapolation the

optimum programmed temperature rate was approximately 14 or 15 deg/min for column lengths of 0.5 meters to 3.0 meters. The optimum rate was difficult to deduce for the 5.0 meter column. For the same range of programmed temperature rates (0.0 to 13.0 deg/min) and for the same pair of compounds (n-nonane-decane) the optimum column length shifted from 1.2 meters (isothermal) to 2.0 meters (13.0 deg/min) for the 20.3 ml/min helium flow rate and from 1.2 meters (isothermal) to 1.6 meters (13.0 deg/min) for the 13.5 ml/min helium flow rate. All of these column lengths are approximations. There was no shift in optimum column length for the 6.8 ml/min helium flow rate. The higher the helium flow rate the more was the shift in optimum column length.

For the separation of n-decane-hendecane the resolution for all three helium flow rates and for all the column lengths, increased gradually as the programmed temperature rate increased from 0.0 deg/min (isothermal) to approximately 11.0 deg/min (optimum) and decreased slightly when the programmed temperature rate increased further from 11.0 deg/min to 13.0 deg/min. For the same range of programmed temperature rates (0.0 to 13.0 deg/min) and for the same pair of compounds (n-decane-hendecane), the optimum column length shifted from 1.6 meters (isothermal) to 2.5 meters (13.0 deg/min) for the 20.3

ml/min helium flow rate, 1.4 meters (isothermal) to 2.5 meters (13.0 deg/min) for the 13.5 ml/min helium flow rate and 1.2 meters (isothermal) to 2.0 meters (13.0 deg/min) for the 6.8 ml/min helium flow rate. All the above optimum column lengths are approximations.

For the separation of n-hendecane-dodecane the resolution for all three helium flow rates in the column length range 0.5 meters to 3.0 meters, increased gradually as the programmed temperature rate increased from 0.0 deg/min (isothermal) to approximately 4.0 deg/min (optimum) and decreased when the programmed temperature rate increased further from 4.0 deg/min to 13.0 deg/min. For the 5.0 meter column the optimum programmed temperature rate shifted from approximately 4.0 deg/min to 6.0 deg/min as the helium flow rate decreased from 20.3 ml/min to 6.8 ml/min. For the same range of programmed temperature rates (0.0 to 13.0 deg/min) and for the same pair of compounds (n-hendecane-dodecane), the optimum column length shifted from 2.0 meters (isothermal) to 3.0 meters (13.0 deg/min) for the 20.3 ml/min helium flow rate, 1.8 meters (isothermal) to 3.0 meters (13.0 deg/min) for the 13.5 ml/min helium flow rate and 1.5 meters (isothermal) to beyond 5.0 meters (13.0 deg/min) for the 6.8 ml/min helium flow rate. All of the above optimum column lengths are also approximations.

4 Time Normalization With Net Retention Time For N-Dodecane Fixed at 800 ± 10 Seconds

Figs. 7 and 8 show the effect of helium flow rate, column length, isothermal temperature, and programmed temperature rate on the resolution of n-nonane, n-decane, n-hendecane, and n-dodecane when the net retention time for n-dodecane was fixed at 800 ± 10 seconds.

The three helium flow rates used were again 6.8, 13.5 and 20.3 ml/min. In all the cases shown the resolution increased as the helium flow rate increased from 6.8 ml/min to 20.3 ml/min at spaced ml/min intervals.

With an increase of helium flow rate from 6.8 ml/min to 13.5 ml/min the percent increase in resolution was dependent on column length and hydrocarbon number. For column lengths 1.0 meter to 5.0 meters the increases in resolution for n-nonane-decane, n-decane-hendecane and n-hendecane-dodecane were approximately 2.0, 1.5 and 0.75 units. For column length 0.5 meters the increases in resolution for the same series of compounds were approximately 1.0, 0.75 and 0.5 units.

For an increase of helium flow rate from 13.5 ml/min to 20.3 ml/min the percent increase in resolution was also dependent on column length and hydrocarbon number. For column lengths 1.0 meter to 5.0 meters the increases in resolution for n-nonane-decane, n-decane-hendecane,

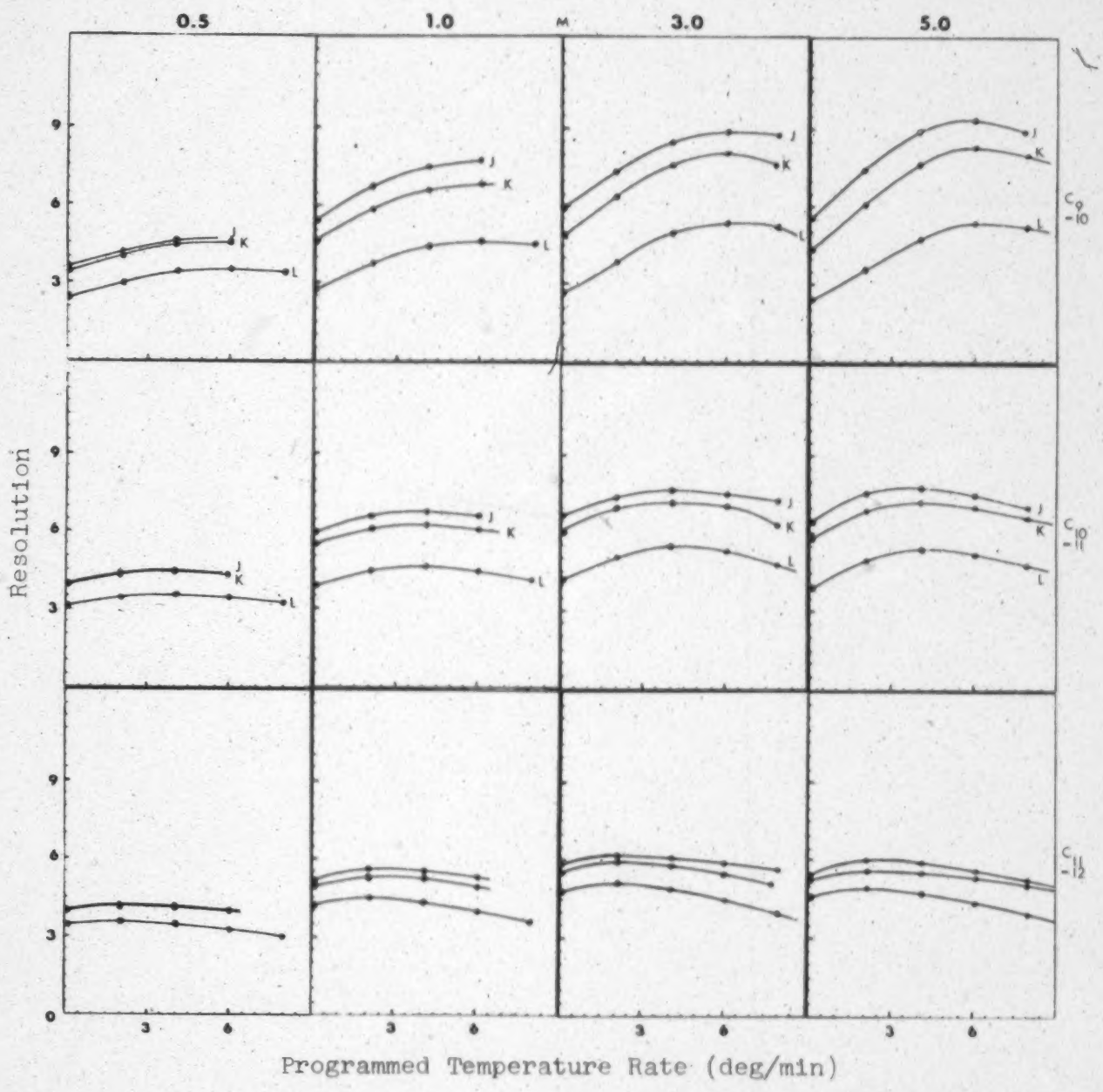

Fig. 7 Resolution vs programmed temperature rate when normalized net retention time for n-dodecane was fixed at 800 ± 10 seconds. Columns from left to right are for column lengths of 0.5, 1.0, 3.0, and 5.0 meters. Rows from top to bottom are for n-nonane-decane, n-decane-hendecane and n-hendecane-dodecane. J, K and L are for helium flow rates of 20.3, 13.5 and 6.8 ml/min.

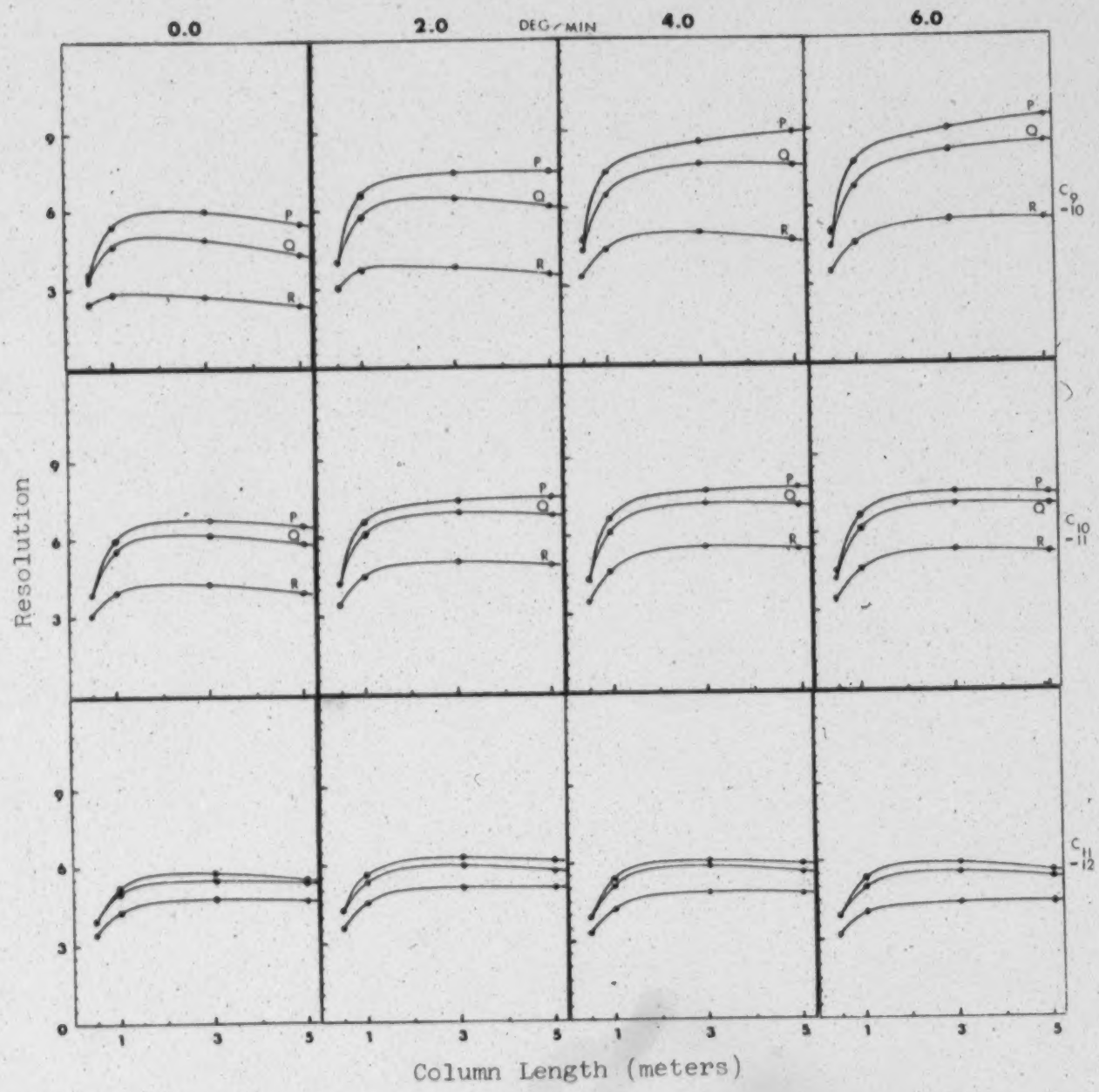

Fig. 8 Resolution vs column length when normalized net retention time for n-dodecane was fixed at 800 ± 10 sec. Columns from left to right are for 0.0 (isothermal), 2.0, 4.0, and 6.0 deg/min. Rows from top to bottom are for n-nonane-decane, n-decane-hendecane and n-hendecane-dodecane. P, Q and R are for helium flow rates of 20.3, 13.5 and 6.8 ml/min.

and n-hendecane-dodecane were approximately 1.0, 0.5 and 0.25 units. For column length 0.5 meters the increase in resolution for n-nonane-decane was approximately 0.2 units and was insignificant for n-decane-hendecane and n-hendecane-dodecane. For a given increase in helium flow rate in the 6.8 ml/min to 20.3 ml/min range, the increase in resolution became more dramatic as the straight chain hydrocarbon number decreased. For a given pair of straight chain hydrocarbons and for a given increase in helium flow rate in the 6.8 ml/min to 20.3 ml/min range, the percent increase in resolution was independent of column length within the 1.0 meter to 5.0 meter range.

For the separation of a given pair of straight chain hydrocarbons, for a given helium flow rate (6.8 to 20.3 ml/min) and for a given programmed temperature rate (0.0 to 6.0 deg/min) the resolution varied by less than one unit when the column length varied from approximately 1.5 meters to 5.0 meters. The resolution dropped sharply by several units when the column length decreased from approximately 1.5 meters to 0.5 meters i.e. when the percent liquid phase increased from approximately 19 to 50 percent.

The optimum programmed temperature rate was dependent on which pair of straight chain hydrocarbons was being

separated. As the straight chain hydrocarbon number increased the optimum programmed temperature rate decreased. For the separation of n-nonane-decane the resolution for all three helium flow rates and all the column lengths increased with programmed temperature rate from 0.0 deg/min (isothermal) to 6.0 deg/min (optimum). For the same range of programmed temperature rates (0.0 to 6.0 deg/min) and for the same pair of compounds (n-nonane-decane) the optimum column length shifted from 2.3 meters (isothermal) to beyond 5.0 meters (6.0 deg/min) for the 20.3 ml/min helium flow rate, 2.0 meters (isothermal) to beyond 5.0 meters (6.0 deg/min) for the 13.5 ml/min helium flow rate and 1.5 meters (isothermal) to 4.0 meters (6.0 deg/min) for the 6.8 ml/min helium flow rate. All of these column lengths are approximations. Close observation of the graphs showed that the higher the helium flow rate the more was the shift in optimum column length.

For the separation of n-decane-hendecane the resolution for all the helium flow rates and all the column lengths, increased as the programmed temperature rate increased from 0.0 deg/min (isothermal) to 4.0 deg/min (optimum) and decreased when the programmed temperature rate increased further from 4.0 deg/min to 6.0 deg/min. For the same range of programmed temperature rates (0.0 to 6.0 deg/min) and for the same pair of compounds

(n-decane-hendecane), the optimum column length shifted from 2.8 meters (isothermal) to 5.0 meters (6.0 deg/min) for the 20.3 ml/min helium flow rate, 2.8 meters (isothermal) to 4.0 meters (6.0 deg/min) for the 13.5 ml/min helium flow rate and 2.5 meters (isothermal) to 3.5 meters (6.0 deg/min) for the 6.8 ml/min helium flow rate. All the above optimum column lengths are approximations.

For the separation of n-hendecane-dodecane the resolution for all three helium flow rates and all the column lengths, increased as the programmed temperature rate increased from 0.0 deg/min (isothermal) to 2.0 deg/min (optimum) and decreased when the programmed temperature rate increased further from 2.0 deg/min to 6.0 deg/min. For the same range of programmed temperature rates (0.0 to 6.0 deg/min)and for the same pair of compounds (n-hendecane-dodecane), the optimum column length remained fixed at approximately 3.0 meters for the 20.3 and 13.5 ml/min helium flow rate and at approximately 4.0 meters for the 6.8 ml/min helium flow rate.

5 Time Normalization With Net Retention Time For N-Dodecane Fixed at 1600 ± 15 Seconds

Figs. 9 and 10 show the effect of helium flow rate, column length, isothermal temperature, and programmed temperature rate on the resolution of n-nonane, n-decane, n-hendecane, and n-dodecane when the net retention time for n-dodecane was fixed at 1600 ± 15 seconds. Fig. 9 is incomplete because as pointed out in the introduction initial column temperatures were restricted to those above room temperature.

The three helium flow rates used were again 6.8, 13.5 and 20.3 ml/min. In all the cases shown the resolution increased with helium flow rate from 6.8 ml/min to 20.3 ml/min at spaced ml/min intervals. With an increase in helium flow rate from 6.8 ml/min to 13.5 ml/min the percent increase in resolution was dependent on column length and the hydrocarbon number. For column lengths 1.0 meter to 5.0 meters the increases in resolution for n-nonane-decane, n-decane-hendecane, and n-hendecane-dodecane, were approximately 2.0, 1.25 and 0.5 units. For column length 0.5 meters the increases in resolution for the same series of compounds were approximately 1.0, 0.75 and 0.5 units.

For an increase of helium flow rate from 13.5 ml/min to 20.3 ml/min the percent increase in resolution was also dependent on column length and the hydrocarbon number.

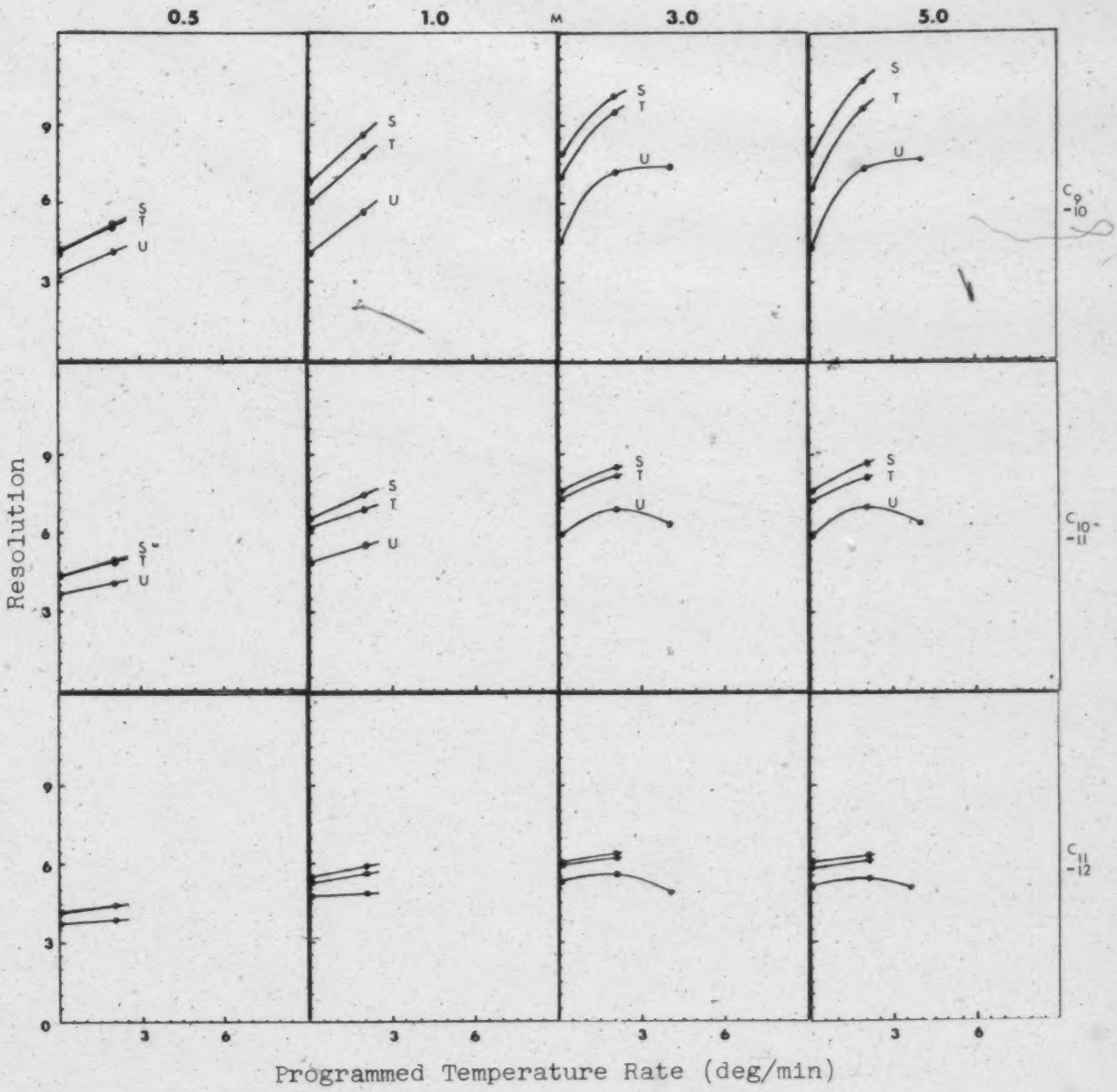

Fig. 9 Resolution vs programmed temperature rate when normalized net retention time for n-dodecane was fixed at 1600 ± 15 seconds. Columns from left to right are for column lengths of 0.5, 1.0, 3.0, and 5.0 meters. Rows from top to bottom are for n-nonane-decane, n-decane-hendecane and n-hendecane-dodecane. S, T and U are for helium flow rates of 20.3, 13.5 and 6.8 ml/min.

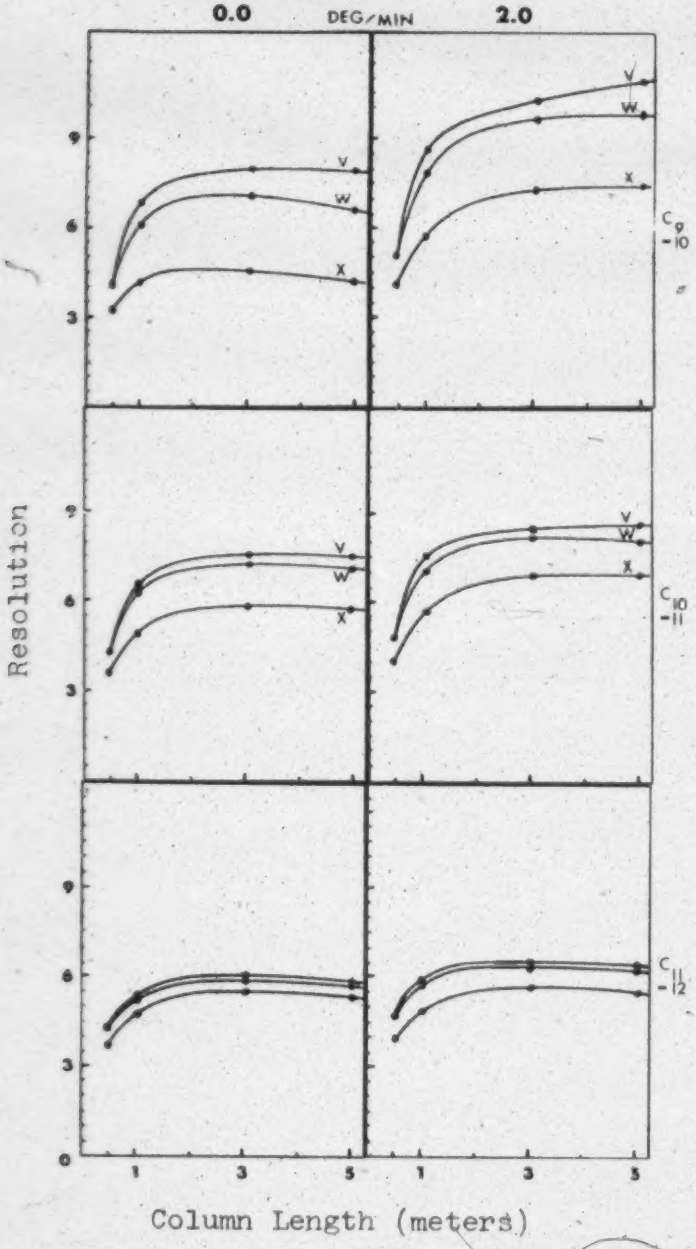

Fig. 10 Resolution vs column length when normalized net retention time for n-dodecane was fixed at 1600 ± 15 sec. Columns from left to right are for 0.0 (isothermal) and 2.0 deg/min. Rows from top to bottom are for n-nonane-decane, n-decane-hendecane and n-hendecane-dodecane. V, W and X are for helium flow rates of 20.3, 13.5 and 6.8 ml/min.

For column lengths 1.0 meter to 5.0 meters, the increases in resolution for n-nonane-decane, n-decane-hendecane and n-hendecane-dodecane were approximately 0.75, 0.35 and 0.2 units. For column length 0.5 meters the increase in resolution for the same series of compounds was insignificant. For a given increase in helium flow rate in the 6.8 ml/min to 20.3 ml/min range, the increase in resolution became more dramatic as the hydrocarbon number decreased. For a given pair of straight chain hydrocarbons and for a given increase in helium flow rate in the 6.8 ml/min to 20.3 ml/min range, the percent increase in resolution was independent of column length within the 1.0 meter to 5.0 meter range.

For the separation of a given pair of straight chain hydrocarbons, for a given helium flow rate (6.8 to 20.3 ml/min) and for a given programmed temperature rate (0.0 to 2.0 deg/min), the resolution varied by less than one unit when the column length varied from approximately 1.5 meters to 5.0 meters. The resolution dropped sharply by several units when the column length decreased from approximately 1.5 meters to 0.5 meters i.e. when the percent liquid phase increased from approximately 19 to 50 percent.

For the separation of n-nonane-decane the resolution for all three helium flow rates and all the column lengths

increased as the programmed temperature rate increased from 0.0 deg/min (isothermal) to 2.0 deg/min. By extrapolation the optimum programmed rate for the 6.8 ml/min helium flow rate (column length 3.0 meters to 5.0 meters) was approximately 4.0 deg/min. The optimum programmed rate for the other two helium flow rates could not be determined. For the same range of programmed temperature rates (0.0 to 2.0 deg/min) and for the same pair of compounds (n-nonane-decane) the optimum column length shifted from 3.5 meters (isothermal) to beyond 5.0 meters (2.0 deg/min) for the 20.3 ml/min helium flow rate, 2.5 meters (isothermal) to 5.0 meters (2.0 deg/min) for the 13.5 ml/min helium flow rate and 2.0 meters (isothermal) to 5.0 meters (2.0 deg/min) for the 6.8 ml/min helium flow rate. All of these column lengths are approximations. Here again the higher the helium flow rate the more the shift in optimum column length.

For the separation of n-decane-hendecane the resolution for all the helium flow rates and all the column lengths increased as the programmed temperature rate increased from 0.0 deg/min (isothermal) to 2.0 deg/min. The optimum programmed temperature rate for the 6.8 ml/min helium flow rate (column length 3.0 meters to 5.0 meters) was approximately 2.0 deg/min. The optimum programmed temperature rate for the other two helium flow rates could not be determined. For the same range

of programmed temperature rates (0.0 to 2.0 deg/min) and for the same pair of compounds (n-decane-hendecane) the optimum column length shifted from 4.0 meters (isothermal) to 5.0 meters (2.0 deg/min) for the 20.3 ml/min helium flow rate, there was no significant shift in optimum column length for the 13.5 ml/min helium flow rate and shifted from 3.5 meters (isothermal) to 4.0 meters (2.0 deg/min) for the 6.8 ml/min helium flow rate. All the above optimum column lengths are again approximations.

For the separation of n-hendecane-dodecane the resolution for all three helium flow rates and all the column lengths, increased as the programmed temperature rate increased from 0.0 deg/min (isothermal) to 2.0 deg/min. The optimum programmed temperature rate for the 6.8 ml/min helium flow rate (column length 3.0 meters to 5.0 meters) was approximately 2.0 deg/min. The optimum programmed temperature rate for the other two helium flow rates could not be determined. For the same range of programmed temperature rates (0.0 to 2.0 deg/min) and for the same pair of compounds, there was no shift in the optimum column length when the programmed temperature rate increased from 0.0 deg/min (isothermal) to 2.0 deg/min for all three helium flow rates.

6 Comparison of Experimental and Theoretical Curves

Figure 11 shows the experimental and theoretical resolution between n-hendecane and n-dodecane versus column length for three (300, 800 and 1600 seconds) normalized net retention times and three (6.8, 13.5 and 20.3 ml/min) helium flow rates for isothermal column temperatures. R is the resolution calculated from the equation

$$R = (t_{R2}-t_{R1})/0.5(w_1+w_2) \qquad \text{Eq. 1}$$

where t_{R1} and w_1 are the net retention time and peak width for the first peak and t_{R2} and w_2 are the net retention time and peak width for the second peak (5). R1 is the resolution calculated from the equation

$$R1 = 1/4\sqrt{L/H_2}\,(\alpha-1/\alpha)(k_2/k_2+1) \qquad \text{Eq. 2}$$

the parameters of which are defined in the introduction. R_{TH1} is the theoretical resolution calculated from the equation derived by Grushka, Yepes-Baraya and Cooke (3)

$$R_{TH1} = \frac{1/4\sqrt{L}\,k_2(\alpha-1/\alpha)}{\sqrt{\frac{2\gamma D_g t_{R2}(k_2+1)}{L} + \frac{2L(\%)^2 k_2(k_2+1)}{3D_1 t_{R2}(S\rho_s)^2}}} \qquad \text{Eq. 3}$$

The above equation was modified and used to calculate another theoretical resolution R_{TH2} where R_{TH2} =

$$\frac{1/4\sqrt{L}\,k_2(\alpha-1/\alpha)}{\sqrt{\frac{2\gamma D_g t_{R2}(k_2+1)}{L} + \frac{2L(\%)^2\sqrt{k_2+1}}{3D_1 t_{R2}(S\rho_s)^2} + \frac{\log(1+L/15)2(k_2)\left(\frac{t_{R2}+(t_{R2})^{0.9}}{t_{R2}}\right)}{(k_2)^{0.7}}}} \qquad \text{Eq. 4}$$

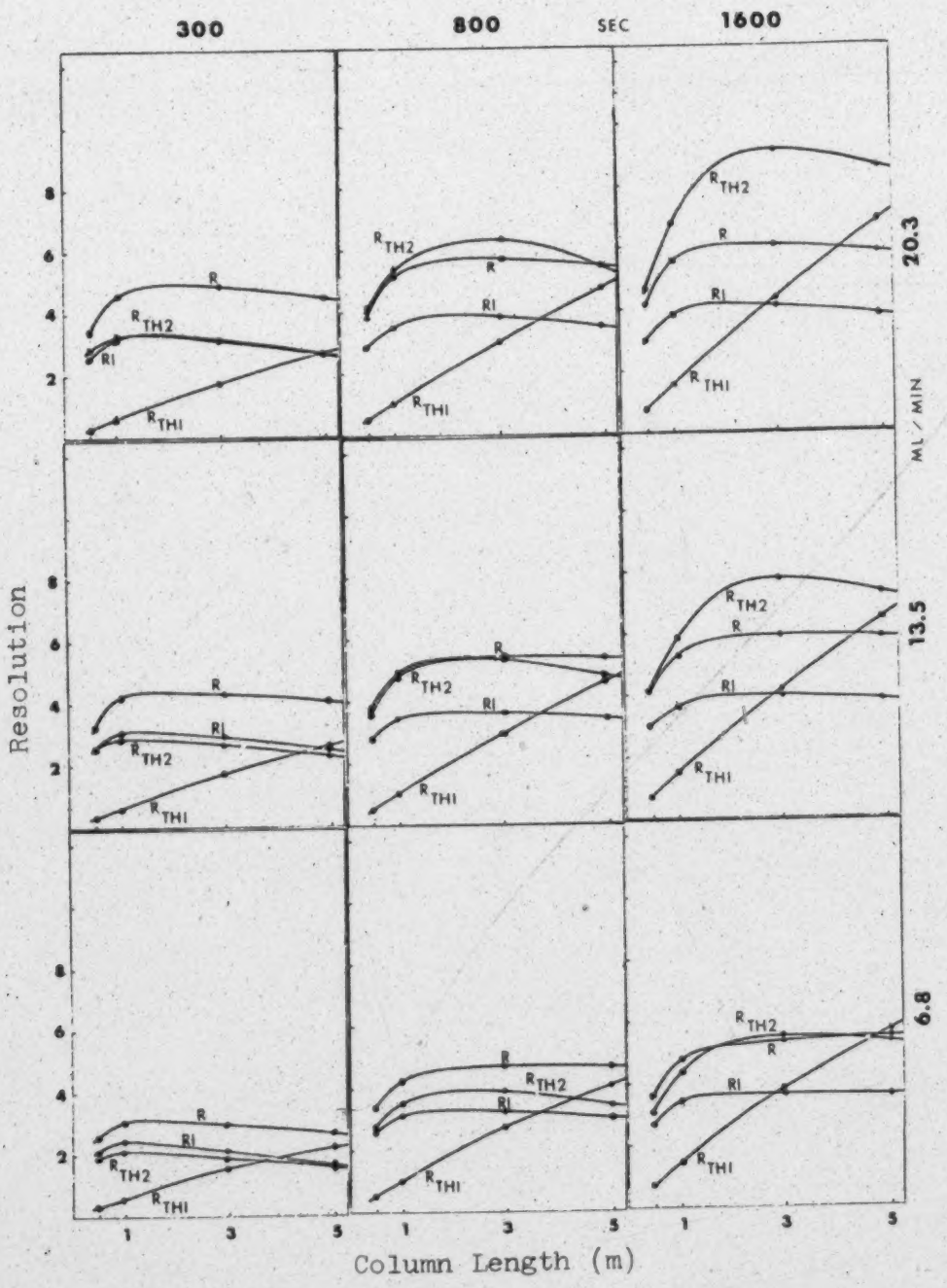

Fig. 11 Resolution between n-hendecane and n-dodecane for normalized net retention times of 300, 800 and 1600 seconds and helium flow rates of 6.8, 13.5 and 20.3 ml/min. The equations for the four curves are R = Equation 1, RI = Equation 2, R_{TH1} = Equation 3, and R_{TH2} = Equation 4. All the curves are for isothermal conditions.

which gives a curve more related to the experimental results of this work. This equation was obtained by trial and error using the second computer program in the appendix.

The curve R_{TH1} in Figure 11 is an approximate straight line the slope of which increases with normalized net retention time. The experimental resolution R or R1 on the other hand increases sharply with column length to about 1.5 meters and then levels off and decreases slightly with increasing column length. It was decided to add a third term to the denominator in Equation 3 which would increase the resolution at short column length and decrease resolution at longer column length. This was first partly overcome by making the second term in the denominator of Equation 3 less dependent on k_2 since k_2 decreases sharply with increasing column length (see Tables 1 and 2). The factors $k_2(k_2+1)$ in the second term were replaced by $(k_2+1)^{1/2}$. Since k_2 changes so rapidly with column length, it was decided that k_2 should be an important factor in the third term. To minimize the rapid decrease of k_2 with increasing column length the third term took the form of a ratio k_2/k_2 each k_2 to a different power. Since the experimental resolution R or R1 is also dependent on the normalized net retention time it was decided that the k_2 in the numerator of the third term should be to

some power involving t_{R2}. To minimize the large numerical change in t_{R2}, this power also took the form of a ratio t_{R2}/t_{R2} each t_{R2} to a different power if necessary. The final form of this ratio was $(t_{R2}+(t_{R2})^{0.9})/t_{R2}$. To introduce a curvature into the curve in the vicinity of column length of 1.5 meters it was decided to use a log factor which was a function of column length. The final form of this factor was $\log(1+L/15)$. Since the experimental resolution is also a function of helium flow rate, this was best overcome by multiplying the first term in the denominator of Equation 3 by the compressibility correction factor j. Thus the end result was Equation 4. It is obvious that there is still a lot of room for improvement. Referring to Figure 11, R_{TH2} increases too rapidly with increasing helium flow rate at long normalized net retention times. This leads one to speculate that the third term (or even the first or second term or possibly a fourth term) in the denominator of Equation 4 should contain yet another factor e.g. the compressibility factor j as a function of normalized net retention time t_{R2}.

The relevant data used to calculate the curves in Fig. 11 are shown in Tables 1 and 2. The constants which were also used are S = 14500. cm^2/gm, ρ_s = 0.240 gm/cc, M_1 = 4.0, M_2 = 170.34, T_{c1} = 5.3 °K, T_{c2} = 659.0 °K, V_{c1} = 57.8 cc/g mole, and V_{c2} = 718. cc/g mole.

Table 1 The relevant data used to calculate the curves in Fig. 11.

Helium Flow Rate (ml/min)	Column Length (cm)	% Liquid Phase (%)	t_{R2} (sec)	α	P_1 (atm)	j	T (°C)	k_2	Resolution R_{TH2}
6.8	50.0	50.0	300.2	1.780	1.026	0.945	133.7	28.5	1.92
6.8	100.0	25.0	300.8	1.779	1.13	0.894	136.7	13.04	2.13
6.8	300.0	8.33	300.3	1.715	1.43	0.771	149.2	3.58	1.89
6.8	500.0	5.0	298.0	1.681	1.94	0.617	153.0	1.76	1.57
13.5	50.0	50.0	299.0	1.874	1.10	0.908	116.0	41.07	2.59
13.5	100.0	25.0	300.0	1.856	1.30	0.821	122.3	18.75	2.85
13.5	300.0	8.33	296.8	1.776	1.98	0.609	135.9	5.62	2.64
13.5	500.0	5.0	302.5	1.761	2.60	0.486	140.5	2.91	2.29
20.3	50.0	50.0	300.0	1.922	1.18	0.873	107.2	43.9	2.82
20.3	100.0	25.0	299.8	1.910	1.48	0.752	114.5	21.66	3.26
20.3	300.0	8.33	299.0	1.813	2.29	0.541	128.5	7.14	3.15
20.3	500.0	5.0	301.2	1.789	2.97	0.433	133.7	3.57	2.65
6.8	50.0	50.0	800.3	1.919	1.026	0.945	108.5	77.28	2.78
6.8	100.0	25.0	798.0	1.895	1.13	0.894	112.0	37.25	3.53
6.8	300.0	8.33	802.0	1.841	1.43	0.771	122.5	10.8	3.88
6.8	500.0	5.0	797.8	1.824	1.94	0.617	124.9	5.31	3.43
13.5	50.0	50.0	801.8	2.018	1.10	0.908	93.4	110.98	3.71
13.5	100.0	25.0	794.4	1.982	1.30	0.821	98.9	54.96	4.82

Table 2 Continuation of Table 1.

Helium Flow Rate (ml/min)	Column Length (cm)	% Liquid Phase (%)	t_{R2} (sec)	α	P_i (atm)	J	T (°C)	k_2	Resolution R_{TH2}
13.5	300.0	8.33	796.2	1.905	1.98	0.609	110.3	15.96	5.31
13.5	500.0	5.0	805.6	1.890	2.60	0.486	114.2	8.22	4.75
20.3	50.0	50.0	804.6	2.074	1.18	0.873	85.0	121.55	4.13
20.3	100.0	25.0	802.4	2.043	1.48	0.752	91.8	58.37	5.34
20.3	300.0	8.33	800.6	1.945	2.29	0.541	103.5	19.9	6.3
20.3	500.0	5.0	801.1	1.918	2.97	0.433	108.9	9.85	5.42
6.8	50.0	50.0	1598.9	2.02	1.026	0.945	93.0	159.87	3.24
6.8	100.0	25.0	1599.4	1.999	1.13	0.894	96.0	76.06	4.32
6.8	300.0	8.33	1607.4	1.944	1.43	0.771	105.6	21.58	5.51
6.8	500.0	5.0	1601.8	1.917	1.94	0.617	108.0	10.83	5.32
13.5	50.0	50.0	1606.5	2.123	1.10	0.908	79.0	237.1	4.36
13.5	100.0	25.0	1597.4	2.088	1.30	0.821	83.9	109.73	5.81
13.5	300.0	8.33	1602.8	2.009	1.98	0.609	94.3	32.42	7.75
13.5	500.0	5.0	1589.8	1.989	2.60	0.486	98.2	16.02	7.27
20.3	50.0	50.0	1610.1	2.187	1.18	0.873	72.0	245.47	4.72
20.3	100.0	25.0	1605.1	2.147	1.48	0.752	77.7	123.98	6.67
20.3	300.0	8.33	1612.3	2.054	2.29	0.541	88.5	39.13	9.12
20.3	500.0	5.0	1604.6	2.022	2.97	0.433	93.2	19.83	8.54

The relative retention ratio α was calculated from the net retention times of n-dodecane and n-hendecane i.e. $\alpha = t_{R2}/t_{R1}$. The compressibility factor j was calculated from the equation $j = 3/2(((P_i/P_o)^2-1)/((P_i/P_o)^3-1))$ where P_o is the outlet column pressure and P_i is the inlet column pressure (6). The inlet column pressure was measured with a Matheson P/N 63-4111 pressure gauge to which had been attached a pressure line and needle. This was inserted through the rubber septum.

The diffusion coefficient of a solute in the gas phase was calculated from the formula (7)

$$D_g = \frac{0.43(T/100)^{1.81}((1/M_1)+(1/M_2))^{0.5}}{P(T_{c1}T_{c2}/10000)^{0.1405}((V_{c1}/100)^{0.4}+(V_{c2}/100)^{0.4})^2}$$

where T is the absolute temperature in °K, P is the column outlet pressure (8), M_1 and M_2 are the molecular weights, T_{c1} and T_{c2} are the critical temperatures in °K, and V_{c1} and V_{c2} are the critical volumes in cm^3/g mole of the eluent gas and diffusing solute.

The value of D_l was obtained by using the assumption that $D_l = 10^{-5}D_g$. The obstruction factor γ was given a value of 0.6.

When the dead volumes i.e. the retention volume of the air peak for the three helium flow rates were extrapolated to zero column length the new dead volumes were 6.01, 5.62 and 4.90 mls (retention times 53.0, 25.0 and 14.5 seconds) for the 6.8, 13.5 and 20.3 ml/min helium

flow rates. These new dead volumes represented the total dead volume of the gas chromatographic system minus the dead volume of the columns. The formulas used to calculate the capacity ratio k_2 for the 6.8, 13.5 and 20.3 ml/min helium flow rates were

$k_2 = (V-V_{ds}-53.0)/(V_{ds}-53.0)$,

$k_2 = (V-V_{ds}-25.0)/(V_{ds}-25.0)$ and

$k_2 = (V-V_{ds}-14.5)/(V_{ds}-14.5)$

where V is the retention time (seconds) of n-dodecane and V_{ds} is the retention time (seconds) of the air peak.

7 General Conclusions When Using Programmed Temperature Time Normalization

1) Resolution increased with helium flow rate. This observation was independent of the normalized retention time, column length and hydrocarbon number.

2) For a given pair of straight chain hydrocarbons and for a given increase in helium flow rate in the 6.8 to 20.3 ml/min range, the percent increase in resolution was the same for column lengths from 1.0 to 5.0 meters but was different for the 0.5 meter column length. This observation was also independent of the normalized retention time.

3) For an increase in helium flow rate from 6.8 to 13.5 ml/min the percent increase in resolution was dependent on column length from 0.5 to 1.0 meter. The increase in resolution was also dependent on the hydrocarbon number for net retention times of 800 ± 10 and 1600 ± 15 seconds but not for 300 ± 5 seconds.

4) For an increase in helium flow rate from 13.5 to 20.3 ml/min the percent increase in resolution was dependent on column length from 0.5 to 1.0 meter and on the hydrocarbon number. This was the case for all net retention times from 300 ± 5 seconds to 1600 ± 15 seconds.

5) For a given increase in helium flow rate in the 6.8 to 20.3 ml/min range, the percent increase in resolution became more dramatic as the hydrocarbon number decreased.

6) For the separation of a given pair of straight chain hydrocarbons, for a given helium flow rate (6.8 to 20.3 ml/min) and for a given programmed temperature rate (0.0 to 13.0 deg/min, 0.0 to 6.0 deg/min and 0.0 to 2.0 deg/min for normalized net retention times of 300 ± 5, 800 ± 10 and 1600 ± 15 seconds), the resolution varied by less than one unit when the column length varied from approximately 1.5 to 5.0 meters.

7) For normalized net retention times of 300 ± 5 to 1600 ± 15 seconds, the resolution dropped sharply by several units when the column length decreased from approximately 1.5 to 0.5 meters i.e. when the percent liquid phase increased from approximately 19 to 50 percent.

8) The optimum programmed temperature rate was dependent on which pair of compounds was being examined. As the straight chain hydrocarbon number increased the optimum programmed temperature rate decreased. Also, for a given pair of hydrocarbons, the optimum programmed temperature rate decreased as the net retention time increased up to about 1600 seconds; here there was indication that the limiting optimum programmed temperature rate was approximately 2.0 deg/min.

9) Generally the higher the helium flow rate the more was the shift to higher values in the optimum column length.

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APPENDIX

Computer program for the calculation of HETP and resolution

Prologue

The computer program written in Fortran can be divided into three major Do loops. The first loop incorporates the entire programm except for the first few cards. The second loop is within the first loop and the third loop is within the second.

The data for this program was obtained from a printer which was connected to a digital integrator which in turn was connected to the detector through a Gow-Mac power supply. A change of 1 mv in the detector would give a response of 1000 counts on the integrator. The system was set up so that the integrator would integrate for 2 seconds, print out the total number of counts, reset the integrator to zero and repeat the process. In this way a numerical outline of a chromatogram could be obtained. If the timer (built into the integrator) was started at the point of injection of a sample, the time (in seconds) as well as the number of counts could both be utilized by the computer program.

Two cards are read into the computer before the first Do loop. Card 1 contains the following information. Columns 1-5 contain an integer which indicates how many data numbers will appear on each card when the base line and numerical outline of the chromatogram are read into the computer. For this program this number can be either

8,15 or 16. The base line and peak outline will be mentioned again later.

Columns 6-10 contain an integer which indicates the number of sets of data (one set of data consists of three injections) that will be read into the computer. This will govern the number of times the first major Do loop will be repeated. The next four numbers must be real numbers.

Columns 11-20 contain the helium flow rate (ml/min).

Columns 21-30 contain the detector current (ma).

Columns 31-40 contain the injection port temperature (°C).

Columns 41-50 contain the sample size (μl).

Columns 1-48 on the second card to be read in will contain the names of the sample components (a maximum of of 4 components in one computer run) that are being separated. The first component is written in columns 1-12, the second in columns 13-24, the third in columns 25-36, and the fourth in columns 37-48.

Inside the first major Do loop one card is read into the computer. This card contains the following information.

Columns 1-5, 6-10 and 11-15 contain integers of the date (day, month and year).

Columns 16-20 contain either the integer 1 or the integer 2. If it is 1 the the data was obtained under isothermal conditions. If it is 2 then the data was obtained under programmed temperature conditions and the isothermal temperature (columns 26-35) read into the computer is

taken as the initial temperature of the column.

Columns 21-25 contain either of the integers 2, 3 or 4. If it is 2 then the data for only two peaks (two components) will be read into the computer. If it is 3 then the data for three peaks (three components) will be read into the computer. If 4 then the data for four peaks (four components) will be read into the computer. The next five numbers must be real numbers.

Columns 26-35 contain the isothermal temperature (°C) of the column.

Columns 36-45 contain the programmed temperature rate (deg/min).

Columns 46-55 contain the sensitivity of the detector.

Columns 56-65 contain the column length (m) and

Columns 66-75 contain the percent liquid loading in the column.

Inside the second major Do loop three types of data are read into the computer. Columns 1-5 on the first card contain a real number indicating the time (in seconds) of the air peak. Columns 1-5 on the second card contain an integer indicating the number of baseline values (counts) that will be read into the computer. The next card (one or more depending on how much baseline is read into the computer) contains the baseline values. The number of values per card has been previously determined.

Inside the third Do loop four types of data are read into the computer. Columns 1-5 on the first card contain an integer indicating the time in seconds at the beginning of a chromatographic peak. Columns 1-5 on the second card contain an integer indicating the number of peak values that will be read into the computer. One peak value corresponds to one print out of the printer. Columns 1-5 on the third card contain a real number the value of which depends on a combination of several factors. The final value of this number depends on the print rate of the printer and on whether every single one or every second or third or fourth etc. of the print out values of the peak are read into the computer. For example if the print rate of the printer was 1 print per 2 seconds and every single value of the peak print out was read into the computer, the value of this number would be 2, i.e. the total number of print out values from the beginning of the peak to the peak maximum multiplied by 2 and added to the time at the beginning of the peak would give the retention time of that peak. If the peak was very broad so that only every tenth peak value (with print rate = 1 print/2 seconds) need be read into the computer then the value of this number would be 20. The fourth card (one or more) contains the peak values of the chromatogram. The number of peak values per card must be the same as for the baseline values.

The number of times the third Do loop repeats itself depends on the number of peaks or components (maximum of 4) for each injection. If 4 peaks are to be read into the computer then the third Do loop will repeat 4 times. The second Do loop will repeat itself 3 times (for 3 injections). The number of times the first Do loop will repeat depends on the number of sets (each of 3 injections) that will be read into the computer.

Epilogue

The program prints out all the data read into the computer. In addition it will calculate and print out for each injection and also the average of the three injections the following: relative peak areas, retention time of each peak, peak heights, baseline peak width, resolution using the formula $R = (t_{R2}-t_{R1})/0.5(w_1+w_2)$, theoretical plates, and peak skew. It prints out the average retention time of the air peak, average net retention time of each peak, average capacity ratio using the formula $k = (V-V_{ds})/V_{ds}$, HETP using the formula $HETP = 16(t_R/w)^2$, and effective plate number. In addition it prints out miscellaneous information such as the positive and negative slopes of the peaks and the (x,y) coordinates on the peaks used to obtain the slopes. This information proves useful in tracking down the source of any errors that may appear in the output.

```
      REAL X(7000),AREA(12),AVGE(4),BASE(48),RET(12),PEAK(12),M(24)
     C,WWOCT(3),WWNON(3),WWDEC(3),WWHEN(3),RRON(3),RRND(3),RRDH(3),
     CTHPOCT(3),THPNON(3),THPDEC(3),THPHEN(3),TAIR(3),AM(8),AW(8),
     CTA,SKOCT(3),SKNON(3),SKDEC(3),SKHEN(3),AA(16),BB(8),XXX(4,12),
     CYYY(2,12),TRE(4),KPRA(4),WONDH(4),ARONDH(4),CPONDH(4),SKONDH(4),
     CHECNDH(4),EPONDH(4),TPONDH(4),W(24)
      INTEGER T,CARD(20)
      READ(5,200) NFM,NS,HFR,DC,PT,SS
  200 FORMAT(2I5,4F10.2)
      READ(5,1501) (CARD(I),I=1,12)
 1501 FORMAT(12A4)
      DO 900 IA=1,NS
      READ(5,201) IDA1,IDA2,IDA3,KK,KKK,CT,PRA,SE,CL,PLP
  201 FORMAT(5I5,5F10.2)
      GO TO(985,986),KK
  986 WRITE(6,987) IDA1,IDA2,IDA3,PRA,CT
  987 FORMAT('1','DATE=',2X,I2,1X,I2,1X,I2,2X,'PROGRAMMED TEMP RATE=',
     C2X,F5.2,2X,'DEGREES CENTIGRADE PER MINUTE WITH INITIAL TEMP=',F7.2
     C,2X,'DEGREES CENTIGRADE')
      WRITE(6,988) CL,SE
  988 FORMAT('COLUMN LENGTH=',F5.2,1X,'METERS',2X,'SENSITIVITY=',F5.2)
      GO TO 992
  985 WRITE(6,989) IDA1,IDA2,IDA3,CT,CL,SE
  989 FORMAT('1','DATE=',2X,I2,1X,I2,1X,I2,2X,'ISOTHERMAL COLUMN TEMP=',
     CF7.1,1X,'DEGREES CENTIGRADE',2X,'COLUMN LENGTH=',F7.2,1X,'METERS',
     C2X,'SENSITIVITY=',F5.2)
  992 WRITE(6,990) HFR,DC,PT
  990 FORMAT(' HELIUM FLOW RATE=',F7.2,2X,'MLS PER MINUTE',2X,'DETECTOR
     CCURRENT=',F6.1,2X,'MILLIAMPS',2X,'INJECTION PORT TEMP=',F6.1,2X,
     C'DEGREES CENTIGRADE')
      WRITE(6,991) SS,(CARD(I),I=1,12)
  991 FORMAT(' SAMPLE SIZE INJECTED WAS',F6.2,2X,'MICROLITER',2X,12A4)
      WRITE(6,912) PLP
  912 FORMAT(' THIS COLUMN IS',F10.2,2X,'PER CENT UCW98 ON CHROMOSORB
     CWAW 60-80 MESH IN 1/8 INCH CU TUBING')
  915 NI=0
      NH=0
      IP=0
      IS=0
      DO 800 IN=1,3
      READ(5,202) TA
  202 FORMAT(F5.1)
      READ(5,203) ITA
  203 FORMAT(I5)
      IF(NFM.EQ.16) GO TO 1502
      IF(NFM.EQ.15) GO TO 1503
      READ(5,1504) (BASE(I),I=1,ITA)
 1504 FORMAT(8F10.0)
      GO TO 1505
 1502 READ(5,1506) (BASE(I),I=1,ITA)
 1506 FORMAT(16F5.0)
      GO TO 1505
 1503 READ(5,1507) (BASE(I),I=1,ITA)
 1507 FORMAT(15F5.0)
 1505 TAIR(IN)=TA
```

```
      SBASE=0.0
      IT=IN
      DO 801 I=1,ITA
  801 SBASE=SBASE+BASE(I)
      AVBASE=SBASE/ITA
      WRITE(6,802) IN
  802 FORMAT('-','THE BASELINE VALUES (COUNTS) FOR INJECTION',I3)
      WRITE(6,803) (BASE(I),I=1,ITA)
  803 FORMAT(1X,20F6.0)
      WRITE(6,804) AVBASE
  804 FORMAT('THE BASELINE AVERAGE =',F7.0,2X,'SECONDS')
      WRITE(6,805) TA
  805 FORMAT('THE AIR PEAK RETENTION TIME =',F7.2,2X,'SECONDS')
      DO 700 IM=1,KKK
      READ(5,720) I
  720 FORMAT(I5)
      READ(5,721) N
  721 FORMAT(I5)
      READ(5,722) DF
  722 FORMAT(F5.2)
      NNN=I+N-1
      IF(NFM.EQ.16) GO TO 1510
      IF(NFM.EQ.15) GO TO 1511
      READ(5,1512) (X(I),I=I,NNN)
 1512 FORMAT(8F10.0)
      GO TO 1513
 1510 READ(5,1520) (X(I),I=I,NNN)
 1520 FORMAT(16F5.0)
      GO TO 1513
 1511 READ(5,1514) (X(I),I=I,NNN)
 1514 FORMAT(15F5.0)
 1513 GO TO(210,211,212,213),IM
  210 WRITE(6,214) (CARD(I),I=1,3),IT
  214 FORMAT('0',T2,'THE PEAK VALUES (COUNTS) FOR',T32,3A4,T45,
     C'INJECTION',I3)
      GO TO 222
  211 WRITE(6,215) (CARD(I),I=4,6),IT
  215 FORMAT('0',T2,'THE PEAK VALUES (COUNTS) FOR',T32,3A4,T45,
     C'INJECTION',I3)
      GO TO 222
  212 WRITE(6,216) (CARD(I),I=7,9),IT
  216 FORMAT('0',T2,'THE PEAK VALUES (COUNTS) FOR',T32,3A4,T45,
     C'INJECTION',I3)
      GO TO 222
  213 WRITE(6,218) (CARD(I),I=10,12),IT
  218 FORMAT('0',T2,'THE PEAK VALUES (COUNTS) FOR',T32,3A4,T45,
     C'INJECTION',I3)
  222 WRITE(6,219) (X(I),I=T,NNN)
  219 FORMAT(1X,17F7.0)
      WRITE(6,220) N
  220 FORMAT('NUMBER OF CURVE DATA POINTS READ IN=',I5)
      WRITE(6,221) T
  221 FORMAT('TIME AT BEGINNING OF PEAK=',I5,2X,'SECONDS')
      KE=AVBASE
      KB=0
```

```
      DO 704 I=T,NNN
      IF(X(I+1)-X(I))701,702,703
  701 KB=KB+1
      IF(KB.EQ.3) GO TO 705
      GO TO 704
  702 KB=0
      GO TO 704
  703 KB=0
      IF(X(I+1).GT.KE) GO TO 706
      GO TO 704
  706 IP=I+1
      KE=X(I+1)
  704 CONTINUE
  705 NI=NI+1
      PEAK(NI)=X(IP)-AVBASE
      AR=0.0
      NN=T+N-1
      IF(DF.EQ.1.0) GO TO 712
      IF(DF.EQ.0.5) GO TO 713
      DO 707 I=T,NNN
  707 AR=AR+X(I)
      DO 710 I=T,NN
  710 AR=AR+((X(I)+X(I+1))/2.0)*(DF-1.0)
      AR=AR-AVBASE*N*DF
      GO TO 711
  712 DO 714 I=T,NNN
  714 AR=AR+X(I)
      AR=AR-AVBASE*N
      GO TO 711
  713 NB=0
      DO 715 I=T,NNN,2
      NB=NB+1
  715 AR=AR+X(I)
      AR=AR-AVBASE*NB
  711 NH=NH+1
      AREA(NH)=AR
      PK1=PEAK(NI)*0.507
      PK2=PEAK(NI)*0.707
      IR=IR+1
      DO 724 I=T,IP
      IF(PK1.GT.(X(I)-AVBASE)) GO TO 724
      PH1=(PK1-(X(I-1)-AVBASE))/((X(I)-AVBASE)-(X(I-1)-AVBASE))
      YYY(1,IR)=PK1
      XX1=T+((I-1)-T+PH1)*DF
      XXX(1,IR)=XX1
      GO TO 510
  724 CONTINUE
  510 DO 725 I=T,IP
      IF(PK2.GT.(X(I)-AVBASE)) GO TO 725
      PH2=(PK2-(X(I-1)-AVBASE))/((X(I)-AVBASE)-(X(I-1)-AVBASE))
      YYY(2,IR)=PK2
      XX2=T+((I-1)-T+PH2)*DF
      XXX(2,IR)=XX2
      GO TO 511
  725 CONTINUE
```

```
511 DO 726 I=IP,NNN
    IF(PK2.GT.(X(I)-AVBASE)) GO TO 727
    GO TO 726
727 PH3=(PK2-(X(I)-AVBASE))/((X(I-1)-AVBASE)-(X(I)-AVBASE))
    XX3=T+((I-1)-T+1.0-PH3)*DF
    XXX(3,IR)=XX3
    GO TO 512
726 CONTINUE
512 DO 728 I=IP,NNN
    IF(PK1.GT.(X(I)-AVBASE)) GO TO 729
    GO TO 728
729 PH4=(PK1-(X(I)-AVBASE))/((X(I-1)-AVBASE)-(X(I)-AVBASE))
    XX4=T+((I-1)-T+1.0-PH4)*DF
    XXX(4,IR)=XX4
    GO TO 513
728 CONTINUE
513 IS=IS+1
    M(IS)=(PK2-PK1)/(XX2-XX1)
    W(IS)=(M(IS)*XX1-PK1)/M(IS)
    IS=IS+1
    M(IS)=(PK1-PK2)/(XX4-XX3)
    W(IS)=(M(IS)*XX3-PK2)/M(IS)
    RET(NI)=(M(IS-1)*XX2-M(IS)*XX3)/(M(IS-1)-M(IS))
700 CONTINUE
800 CONTINUE
    A=(TAIR(1)+TAIR(2)+TAIR(3))/3.0
    GO TO (223,223,224,225),KKK
225 JB=5
    JE=9
    GO TO 1225
224 JB=4
    JE=7
    GO TO 1225
223 JB=3
    JE=5
1225 NK=0
    DO 1224 I=1,KKK
    TRE(I)=(RET(NK+1)+RET(NK+JB)+RET(NK+JE))/3.0
1224 NK=NK+1
    GO TO (227,227,228,229),KKK
229 JB=5
    JE=9
    GO TO 1229
228 JB=4
    JE=7
    GO TO 1229
227 JB=3
    JE=5
1229 NK=0
    DO 1228 I=1,KKK
    KPEA(I)=(PEAK(NK+1)+PEAK(NK+JB)+PEAK(NK+JE))/3.0
1228 NK=NK+1
    NA=0
    NK=0
    GO TO (231,231,232,233),KKK
```

```
233 JB=5
    JE=9
    GO TO 524
232 JB=4
    JE=7
    GO TO 524
231 JB=3
    JE=5
524 DO 520 I=1,4
    DO 521 J=1,KKK
    NA=NA+1
    AA(NA)=(XXX(I,NK+1)+XXX(I,NK+JB)+XXX(I,NK+JE))/3.0
521 NK=NK+1
    NK=0
520 CONTINUE
    NA=0
    NK=0
    DO 522 I=1,2
    DO 523 J=1,KKK
    NA=NA+1
    BB(NA)=(YYY(I,NK+1)+YYY(I,NK+JB)+YYY(1,NK+JE))/3.0
523 NK=NK+1
    NK=0
522 CONTINUE
    NA=0
    NK=0
    GO TO (235,235,236,237),KKK
237 JI=8
    JB=9
    JE=17
    GO TO 534
236 JI=6
    JB=7
    JE=13
    GO TO 534
235 JI=4
    JB=5
    JE=9
534 DO 532 I=1,JI
    NA=NA+1
    AM(NA)=(M(NK+1)+M(NK+JB)+M(NK+JE))/3.0
    AW(NA)=(W(NK+1)+W(NK+JB)+W(NK+JE))/3.0
532 NK=NK+1
    NB=0
    GO TO (239,239,240,241),KKK
241 DO 962 NA=1,3
    WWOCT(NA)=W(NB+2)-W(NB+1)
    WWNON(NA)=W(NB+4)-W(NB+3)
    WWDEC(NA)=W(NB+6)-W(NB+5)
    WWHEN(NA)=W(NB+8)-W(NB+7)
962 NB=NB+8
    GO TO 242
240 DO 243 NA=1,3
    WWOCT(NA)=W(NB+2)-W(NB+1)
    WWNON(NA)=W(NB+4)-W(NB+3)
```

```
      WWDEC(NA)=W(NB+6)-W(NB+5)
  243 NB=NB+6
      GO TO 242
  239 DO 246 NA=1,3
      WWOCT(NA)=W(NB+2)-W(NB+1)
      WWNON(NA)=W(NB+4)-W(NB+3)
  246 NB=NB+4
  242 GO TO (248,248,249,250),KKK
  250 WONDH(4)=(WWHEN(1)+WWHEN(2)+WWHEN(3))/3.0
  249 WONDH(3)=(WWDEC(1)+WWDEC(2)+WWDEC(3))/3.0
  248 WONDH(2)=(WWNON(1)+WWNON(2)+WWNON(3))/3.0
      WONDH(1)=(WWOCT(1)+WWOCT(2)+WWOCT(3))/3.0
      NB=0
      NK=0
      GO TO (251,251,252,253),KKK
  253 DO 969 NA=1,3
      RRON(NA)=2.0*((RET(NK+2)-RET(NK+1))/(WWOCT(NB+1)+WWNON(NB+1)))
      RRND(NA)=2.0*((RET(NK+3)-RET(NK+2))/(WWNON(NB+1)+WWDEC(NB+1)))
      RRDH(NA)=2.0*((RET(NK+4)-RET(NK+3))/(WWDEC(NB+1)+WWHEN(NB+1)))
      NK=NK+4
  969 NB=NB+1
      GO TO 254
  252 DO 255 NA=1,3
      RRON(NA)=2.0*((RET(NK+2)-RET(NK+1))/(WWOCT(NB+1)+WWNON(NB+1)))
      RRND(NA)=2.0*((RET(NK+3)-RET(NK+2))/(WWNON(NB+1)+WWDEC(NB+1)))
      NK=NK+3
  255 NB=NB+1
      GO TO 254
  251 DO 257 NA=1,3
      RRON(NA)=2.0*((RET(NK+2)-RET(NK+1))/(WWOCT(NB+1)+WWNON(NB+1)))
      NK=NK+2
  257 NB=NB+1
  254 GO TO (258,258,259,260),KKK
  260 RDH=(RRDH(1)+RRDH(2)+RRDH(3))/3.0
  259 RND=(RRND(1)+RRND(2)+RRND(3))/3.0
  258 RON=(RRON(1)+RRON(2)+RRON(3))/3.0
      NB=0
      NK=0
      GO TO (261,261,262,263),KKK
  263 DO 975 NA=1,3
      THPOCT(NA)=16.0*(RET(NB+1)/WWOCT(NK+1))**2
      THPNON(NA)=16.0*(RET(NB+2)/WWNON(NK+1))**2
      THPDEC(NA)=16.0*(RET(NB+3)/WWDEC(NK+1))**2
      THPHEN(NA)=16.0*(RET(NB+4)/WWHEN(NK+1))**2
      NB=NB+4
  975 NK=NK+1
      GO TO 264
  262 DO 265 NA=1,3
      THPOCT(NA)=16.0*(RET(NB+1)/WWOCT(NK+1))**2
      THPNON(NA)=16.0*(RET(NB+2)/WWNON(NK+1))**2
      THPDEC(NA)=16.0*(RET(NB+3)/WWDEC(NK+1))**2
      NB=NB+3
  265 NK=NK+1
      GO TO 264
  261 DO 268 NA=1,3
```

```
      THPOCT(NA)=16.0*(RET(NB+1)/WWOCT(NK+1))**2
      THPNON(NA)=16.0*(RET(NB+2)/WWNON(NK+1))**2
      NB=NB+2
  268 NK=NK+1
  264 GO TO (270,270,271,272),KKK
  272 TPONDH(4)=(THPHEN(1)+THPHEN(2)+THPHEN(3))/3.0
  271 TPONDH(3)=(THPDEC(1)+THPDEC(2)+THPDEC(3))/3.0
  270 TPONDH(2)=(THPNON(1)+THPNON(2)+THPNON(3))/3.0
      TPONDH(1)=(THPOCT(1)+THPOCT(2)+THPOCT(3))/3.0
      GO TO (273,273,274,275),KKK
  275 ARONDH(4)=TRE(4)-A
  274 ARONDH(3)=TRE(3)-A
  273 ARONDH(2)=TRE(2)-A
      ARONDH(1)=TRE(1)-A
      GO TO (276,276,277,278),KKK
  278 CPONDH(4)=(TRE(4)-A)/A
  277 CPONDH(3)=(TRE(3)-A)/A
  276 CPONDH(2)=(TRE(2)-A)/A
      CPONDH(1)=(TRE(1)-A)/A
      NB=0
      NK=0
      GO TO (281,281,282,283),KKK
  283 DO 279 NA=1,3
      SKOCT(NA)=(W(NB+2)-RET(NK+1))/(RET(NK+1)-W(NB+1))
      SKNON(NA)=(W(NB+4)-RET(NK+2))/(RET(NK+2)-W(NB+3))
      SKDEC(NA)=(W(NB+6)-RET(NK+3))/(RET(NK+3)-W(NB+5))
      SKHEN(NA)=(W(NB+8)-RET(NK+4))/(RET(NK+4)-W(NB+7))
      NB=NB+8
  279 NK=NK+4
      GO TO 286
  282 DO 499 NA=1,3
      SKOCT(NA)=(W(NB+2)-RET(NK+1))/(RET(NK+1)-W(NB+1))
      SKNON(NA)=(W(NB+4)-RET(NK+2))/(RET(NK+2)-W(NB+3))
      SKDEC(NA)=(W(NB+6)-RET(NK+3))/(RET(NK+3)-W(NB+5))
      NB=NB+6
  499 NK=NK+3
      GO TO 286
  281 DO 289 NA=1,3
      SKOCT(NA)=(W(NB+2)-RET(NK+1))/(RET(NK+1)-W(NB+1))
      SKNON(NA)=(W(NB+4)-RET(NK+2))/(RET(NK+2)-W(NB+3))
      NB=NB+4
  289 NK=NK+2
  286 GO TO (291,291,292,293),KKK
  293 SKONDH(4)=(SKHEN(1)+SKHEN(2)+SKHEN(3))/3.0
  292 SKONDH(3)=(SKDEC(1)+SKDEC(2)+SKDEC(3))/3.0
  291 SKONDH(2)=(SKNON(1)+SKNON(2)+SKNON(3))/3.0
      SKONDH(1)=(SKOCT(1)+SKOCT(2)+SKOCT(3))/3.0
      GO TO (297,297,298,299),KKK
  299 EPONDH(4)=16.0*((TRE(4)-A)/WONDH(4))**2
  298 EPONDH(3)=16.0*((TRE(3)-A)/WONDH(3))**2
  297 EPONDH(2)=16.0*((TRE(2)-A)/WONDH(2))**2
      EPONDH(1)=16.0*((TRE(1)-A)/WONDH(1))**2
      GO TO (294,294,295,296),KKK
  296 HEONDH(4)=(CI/EPONDH(4))*1000.0
  295 HEONDH(3)=(CI/EPONDH(3))*1000.0
```

```
294 HEONDH(2)=(CL/EPONDH(2))*1000.0
    HEONDH(1)=(CL/EPONDH(1))*1000.0
    NB=0
    GO TO (303,303,304,305),KKK
305 DO 306 NA=1,4
    AVGE(NA)=(AREA(NB+1)+AREA(NB+5)+AREA(NB+9))/3.0
306 NB=NB+1
    GO TO 307
304 DO 308 NA=1,3
    AVGE(NA)=(AREA(NB+1)+AREA(NB+4)+AREA(NB+7))/3.0
308 NB=NB+1
    GO TO 307
303 DO 309 NA=1,2
    AVGE(NA)=(AREA(NB+1)+AREA(NB+3)+AREA(NB+5))/3.0
309 NB=NB+1
307 WRITE(6,903)(CARD(I),I=1,3),(CARD(I),I=4,6),(CARD(I),I=7,9),
   C(CARD(I),I=10,12)
903 FORMAT('-',T33,3A4,T48,3A4,T63,3A4,T80,3A4)
    NB=0
    DO 904 NA=1,3
    WRITE(6,905)NA,(AREA(NB+I),I=1,KKK)
904 NB=NB+KKK
    WRITE(6,906)(AVGE(I),I=1,KKK)
905 FORMAT(T12,'AREA (TOTAL COUNTS)=',
   CT99,'INJECTION',I3,T33,F10.0,T48,F10.0,T63,F10.0,T80,F10.0)
906 FORMAT(T19,'AVERAGE AREA=',
   CT33,F10.0,T48,F10.0,T63,F10.0,T80,F10.0)
    NB=0
    DO 920 NA=1,3
    WRITE(6,318)NA,(RET(NB+I),I=1,KKK)
920 NB=NB+KKK
    WRITE(6,922)(TRE(I),I=1,KKK)
318 FORMAT(T7,'RETENTION TIME (SECONDS)=',
   CT99,'INJECTION',I3,T34,F7.2,T49,F7.2,T64,F7.2,T81,F7.2)
922 FORMAT(T9,'AVERAGE RETENTION TIME=',
   CT34,F7.2,T49,F7.2,T64,F7.2,T81,F7.2)
    NB=0
    DO 923 NA=1,3
    WRITE(6,924)NA,(PEAK(NB+I),I=1,KKK)
923 NB=NB+KKK
    WRITE(6,925)(KPEA(I),I=1,KKK)
924 FORMAT(T11,'PEAK HEIGHT (COUNTS)=',
   CT99,'INJECTION',I3,T34,F7.0,T49,F7.0,T64,F7.0,T81,F7.0)
925 FORMAT(T12,'AVERAGE PEAK HEIGHT=',
   CT34,F7.0,T49,F7.0,T64,F7.0,T81,F7.0)
    NB=0
    DO 926 NA=1,3
    WRITE(6,927)NA,(XXX(1,NB+I),I=1,KKK)
926 NB=NB+KKK
    WRITE(6,928)(AA(I),I=1,KKK)
927 FORMAT(T18,'X1 COORDINATE=',
   CT99,'INJECTION',I3,T34,F7.2,T49,F7.2,T64,F7.2,T81,F7.2)
928 FORMAT(T10,'AVERAGE X1 COORDINATE=',
   CT34,F7.2,T49,F7.2,T64,F7.2,T81,F7.2)
    NB=0
```

```
      GO TO(340,340,341,342),KKK
  342 JB=5
      JE=8
      GO TO 1342
  341 JB=4
      JE=6
      GO TO 1342
  340 JB=3
      JE=4
 1342 DO 929 NA=1,3
      WRITE(6,930)NA,(XXX(2,NB+I),I=1,KKK)
  929 NB=NB+KKK
      WRITE(6,931)(AA(I),I=JB,JE)
  930 FORMAT(T18,'X2 COORDINATE=',
     CT99,'INJECTION',I3,T34,F7.2,T49,F7.2,T64,F7.2,T81,F7.2)
  931 FORMAT(T10,'AVERAGE X2 COORDINATE=',
     CT34,F7.2,T49,F7.2,T64,F7.2,T81,F7.2)
      NB=0
      GO TO(348,348,349,350),KKK
  350 JB=9
      JE=12
      GO TO 1350
  349 JB=7
      JE=9
      GO TO 1350
  348 JB=5
      JE=6
 1350 DO 932 NA=1,3
      WRITE(6,933)NA,(XXX(3,NB+I),I=1,KKK)
  932 NB=NB+KKK
      WRITE(6,934)(AA(I),I=JB,JE)
  933 FORMAT(T18,'X3 COORDINATE=',
     CT99,'INJECTION',I3,T34,F7.2,T49,F7.2,T64,F7.2,T81,F7.2)
  934 FORMAT(T10,'AVERAGE X3 COORDINATE=',
     CT34,F7.2,T49,F7.2,T64,F7.2,T81,F7.2)
      NB=0
      GO TO (356,356,357,358),KKK
  358 JB=13
      JE=16
      GO TO 1358
  357 JB=10
      JE=12
      GO TO 1358
  356 JB=7
      JE=8
 1358 DO 935 NA=1,3
      WRITE(6,936)NA,(XXX(4,NB+I),I=1,KKK)
  935 NB=NB+KKK
      WRITE(6,937)(AA(I),I=JB,JE)
  936 FORMAT(T18,'X4 COORDINATE=',
     CT99,'INJECTION',I3,T34,F7.2,T49,F7.2,T64,F7.2,T81,F7.2)
  937 FORMAT(T10,'AVERAGE X4 COORDINATE=',
     CT34,F7.2,T49,F7.2,T64,F7.2,T81,F7.2)
      NB=0
      DO 938 NA=1,3
```

```
      WRITE(6,939)NA,(YYY(1,NB+I),I=1,KKK)
  938 NB=NB+KKK
      WRITE(6,940)(BB(I),I=1,KKK)
  939 FORMAT(T11,'Y1 AND Y4 COORDINATE=',
     CT99,'INJECTION',I3,T33,F8.1,T48,F8.1,T63,F8.1,T80,F8.1)
  940 FORMAT(T3,'AVERAGE Y1 AND Y4 COORDINATE=',
     CT33,F8.1,T48,F8.1,T63,F8.1,T80,F8.1)
      NB=0
      GO TO (372,372,373,374),KKK
  374 JB=5
      JE=8
      GO TO 1374
  373 JB=4
      JE=6
      GO TO 1374
  372 JB=3
      JE=4
 1374 DO 941 NA=1,3
      WRITE(6,942)NA,(YYY(2,NB+I),I=1,KKK)
  941 NB=NB+KKK
      WRITE(6,943)(BB(I),I=JB,JE)
  942 FORMAT(T11,'Y2 AND Y3 COORDINATE=',
     CT99,'INJECTION',I3,T33,F8.1,T48,F8.1,T63,F8.1,T80,F8.1)
  943 FORMAT(T3,'AVERAGE Y2 AND Y3 COORDINATE=',
     CT33,F8.1,T48,F8.1,T63,F8.1,T80,F8.1)
      NB=0
      GO TO (396,396,397,398),KKK
  398 JB=7
      GO TO 1398
  397 JB=5
      GO TO 1398
  396 JB=3
 1398 DO 950 NA=1,3
      WRITE(6,951)NA,(M(NB+I),I=1,JB,2)
  950 NB=NB+JB+1
      WRITE(6,952)(AM(I),I=1,JB,2)
  951 FORMAT(T17,'POSITIVE SLOPE=',
     CT99,'INJECTION',I3,T34,F7.0,T49,F7.0,T64,F7.0,T81,F7.0)
  952 FORMAT(T9,'AVERAGE POSITIVE SLOPE=',
     CT34,F7.0,T49,F7.0,T64,F7.0,T81,F7.0)
      NB=0
      GO TO (404,404,405,406),KKK
  406 JB=8
      GO TO 1406
  405 JB=6
      GO TO 1406
  404 JB=4
 1406 DO 953 NA=1,3
      WRITE(6,954)NA,(M(NB+I),I=2,JB,2)
  953 NB=NB+JB
      WRITE(6,955)(AM(I),I=2,JB,2)
  954 FORMAT(T17,'NEGATIVE SLOPE=',
     CT99,'INJECTION',I3,T34,F7.0,T49,F7.0,T64,F7.0,T81,F7.0)
  955 FORMAT(T9,'AVERAGE NEGATIVE SLOPE=',
     CT34,F7.0,T49,F7.0,T64,F7.0,T81,F7.0)
```

```
      NB=0
      GO TO (412,412,413,414),KKK
  414 JB=7
      GO TO 1414
  413 JB=5
      GO TO 1414
  412 JB=3
 1414 DO 956 NA=1,3
      WRITE(6,957)NA,(W(NB+I),I=1,JB,2)
  956 NB=NB+JB+1
      WRITE(6,958)(AW(I),I=1,JB,2)
  957 FORMAT(T4,'POSITIVE BASELINE INTERCEPT=',
     CT99,'INJECTION',I3,T34,F7.2,T49,F7.2,T64,F7.2,T81,F7.2)
  958 FORMAT(T5,'AVERAGE +VE BASE INTERCEPT=',
     CT34,F7.2,T49,F7.2,T64,F7.2,T81,F7.2)
      NB=0
      GO TO (420,420,421,422),KKK
  422 JB=8
      GO TO 1422
  421 JB=6
      GO TO 1422
  420 JB=4
 1422 DO 959 NA=1,3
      WRITE(6,960)NA,(W(NB+I),I=2,JB,2)
  959 NB=NB+JB
      WRITE(6,961)(AW(I),I=2,JB,2)
  960 FORMAT(T4,'NEGATIVE BASELINE INTERCEPT=',
     CT99,'INJECTION',I3,T34,F7.2,T49,F7.2,T64,F7.2,T81,F7.2)
  961 FORMAT(T5,'AVERAGE -VE BASE INTERCEPT=',
     CT34,F7.2,T49,F7.2,T64,F7.2,T81,F7.2)
      NB=0
      GO TO (428,428,429,430),KKK
  430 DO 966 NA=1,3
      WRITE(6,967)NA,WWOCT(NB+1),WWNCN(NB+1),WWDEC(NB+1),WWHEN(NB+1)
  966 NB=NB+1
      GO TO 431
  967 FORMAT(T12,'BASELINE PEAK WIDTH=',
     CT99,'INJECTION',I3,T34,F7.2,T49,F7.2,T64,F7.2,T81,F7.2)
  429 DO 432 NA=1,3
      WRITE(6,967)NA,WWOCT(NB+1),WWNCN(NB+1),WWDEC(NB+1)
  432 NB=NB+1
      GO TO 431
  428 DO 434 NA=1,3
      WRITE(6,967)NA,WWOCT(NB+1),WWNCN(NB+1)
  434 NB=NB+1
  431 WRITE(6,968)(WONDH(I),I=1,KKK)
  968 FORMAT(T4,'AVERAGE BASELINE PEAK WIDTH=',
     CT34,F7.2,T49,F7.2,T64,F7.2,T81,F7.2)
      NB=0
      GO TO (436,436,437,438),KKK
  438 DO 972 NA=1,3
      WRITE(6,973)BRON(NB+1),BRND(NB+1),BRDH(NB+1),NA
  973 FORMAT(T21,'RESOLUTION=',T42,F7.2,T57,F7.2,T72,F7.2,T99,
     C'INJECTION',I3)
  972 NB=NB+1
```

```
      WRITE(6,974)RON,RND,RDH
  974 FORMAT(T13,'AVERAGE RESOLUTION=',T42,F7.2,T57,F7.2,T72,F7.2)
      GO TO 439
  437 DO 440 NA=1,3
      WRITE(6,441)RRON(NB+1),RRND(NB+1),NA
  441 FORMAT(T21,'RESOLUTION=',T42,F7.2,T57,F7.2,T99,'INJECTION',I3)
  440 NB=NB+1
      WRITE(6,974)RON,RND
      GO TO 439
  438 DO 442 NA=1,3
      WRITE(6,443)RRON(NB+1),NA
  443 FORMAT(T21,'RESOLUTION=',T42,F7.2,T99,'INJECTION',I3)
  442 NB=NB+1
      WRITE(6,974)RON
  439 NB=0
      GO TO (444,444,445,446),KKK
  446 DO 979 NA=1,3
      WRITE(6,980)NA,THPOCT(NB+1),THPNON(NB+1),THPDEC(NB+1),THPHEN(NB+1)
  979 NB=NB+1
      GO TO 447
  980 FORMAT(T13,'THEORETICAL PLATES=',
     CT99,'INJECTION',I3,T34,F7.0,T49,F7.0,T64,F7.0,T81,F7.0)
  445 DO 448 NA=1,3
      WRITE(6,980)NA,THPOCT(NB+1),THPNON(NB+1),THPDEC(NB+1)
  448 NB=NB+1
      GO TO 447
  444 DO 450 NA=1,3
      WRITE(6,980)NA,THPOCT(NB+1),THPNON(NB+1)
  450 NB=NB+1
  447 WRITE(6,981)(TPONDH(I),I=1,KKK)
  981 FORMAT(T5,'AVERAGE THFORETICAL PLATES=',
     CT34,F7.0,T49,F7.0,T64,F7.0,T81,F7.0)
      WRITE(6,982)A
  982 FORMAT(T21,'GAS HOLDUP=',F7.2,2X,'SECONDS')
      WRITE(6,983)(ARONDH(I),I=1,KKK)
  983 FORMAT(T8,'ADJUSTED RETENTION TIME=',
     CT99,'AVERAGE',T34,F7.2,T49,F7.2,T64,F7.2,T81,F7.2)
      WRITE(6,984)(CPONDH(I),I=1,KKK)
  984 FORMAT(T4,'CAPACITY OR PARTITION RATIO=',
     CT99,'AVERAGE',T34,F7.2,T49,F7.2,T64,F7.2,T81,F7.2)
      WRITE(6,467)(HEONDH(I),I=1,KKK)
  467 FORMAT(T21,'HETP (MM) =',
     CT99,'AVERAGE',T34,F7.2,T49,F7.2,T64,F7.2,T81,F7.2)
      WRITE(6,474)(EPONDH(I),I=1,KKK)
  474 FORMAT(T9,'EFFECTIVE PLATE NUMBER=',
     CT99,'AVEPAGE',T34,F7.0,T49,F7.0,T64,F7.0,T81,F7.0)
      NB=0
      GO TO (478,478,479,480),KKK
  480 DO 481 NA=1,3
      WRITE(6,482)NA,SKOCT(NB+1),SKNON(NB+1),SKDEC(NB+1),SKHEN(NB+1)
  481 NB=NB+1
      GO TO 1480
  482 FORMAT(T27,'SKEW=',
     CT99,'INJECTION',I3,T34,F7.4,T49,F7.4,T64,F7.4,T81,F7.4)
  479 DO 485 NA=1,3
```

```
      WRITE(6,482)NA,SKOCT(NB+1),SKNCN(NB+1),SKDEC(NB+1)
  485 NB=NB+1
      GO TO 1480
  478 DO 487 NA=1,3
      WRITE(6,482)NA,SKOCT(NB+1),SKNON(NB+1)
  487 NB=NB+1
 1480 WRITE(6,483)(SKCNDH(I),I=1,KKK)
  483 FORMAT(T19,'AVERAGE SKEW=',
     CT34,F7.4,T49,F7.4,T64,F7.4,T81,F7.4)
  900 CONTINUE
      STOP
      END
```

The following is the computer program used to calculate R1, R_{TH1} and R_{TH2}.

```
      REAL T,M1,M2,TC1,TC2,VC1,VC2,DG0,DL,L,K,ALPH,J,TR1,TR2,EXPR1,H,
     CPERC,S,ROHS,PI,PO,PR,PR,X1,X2,X3,X4,Y1,Y2,Y3,Y4,EXPR2,THEORR
     C,Y5,Z1
      INTEGER I
      READ(5,700)S,ROHS,M1,M2,TC1,TC2,VC1,VC2
  700 FORMAT(8F10.3)
      DO 900 I=1,100,1
      READ(5,910)TR1,TR2,PR,PI,PO,T,PR
  910 FORMAT(7F10.3)
      WRITE(6,911)
  911 FORMAT('0',T9,'S',T17,'ROHS',T28,'TR1',T37,'TR2',T47,'PR',
     CT58,'PI',T68,'PO',T78,'PR')
      WRITE(6,912)S,ROHS,TR1,TR2,PR,PI,PO,PR
  912 FORMAT(' ',8F10.3)
      WRITE(6,921)
  921 FORMAT('0',T7,'M1',T17,'M2',T26,'TC1',T36,'TC2',T46,'VC1',
     CT58,'VC2')
      WRITE(6,922)M1,M2,TC1,TC2,VC1,VC2
  922 FORMAT(6F10.3)
      ALPH=TR2/TR1
      J=1.5*((PI/PO)**2-1.0)/((PI/PO)**3-1.0)
      X1=0.43*((T+273.0)/100.0)**1.81
      X2=((1.0/M1)+(1.0/M2))**0.5
      X3=0.92*((TC1*TC2)/10000.0)**0.1405
      X4=(((VC1/100.0)**0.4)+((VC2/100.0)**0.4))**2
      DG0=(X1*X2)/(X3*X4)
      DL=0.00001*DG0
      READ(5,810)L,PERC,K,EXPR1,H
  810 FORMAT(5F10.3)
      Y1=0.25*K*((ALPH-1.0)/ALPH)*L**0.5
      Y2=2*J*0.6*TR2*DG0*(1.0+K)/L
      Y3=0.667*L*(1.0+K)**0.5*PERC**2
      Y4=DL*TR2*K*(S*ROHS)**2
      Z1=(TR2+TR2**0.9)/TR2
      Y5=ALOG10(1.0+L/15)*(2*K**Z1)/K**0.7
      THEORR=Y1/(Y2+Y3/Y4+Y5)**0.5
      EXPR2=0.25*((ALPH-1.0)/ALPH)*(K/(K+1.0))*(L/H)**0.5
      WRITE(6,930)
  930 FORMAT('0',T6,'ITEMP',T18,'DG0',T28,'DL',T38,'J',T47,'ALPH',
     CT58,'K',T64,'PER CENT',T76,'COL L',T85,'THEOR R',T97,'EXP R1',
     CT108,'EXP R2')
      WRITE(6,811)T,DG0,DL,J,ALPH,K,PERC,L,THEORR,EXPR1,EXPR2
  811 FORMAT(' ',F9.3,F9.5,2X,F10.9,8F10.3)
  900 CONTINUE
      STOP
      END
```